CORROSION OF CARBON STEEL

IN DIFFERENT BIODIESEL BLENDS

CHAPTER 1

INTRODUCTION

1.1 Overview on biodiesel

Biodiesel is a domestically produced, renewable fuel that is manufactured from animal fat-based diesel fuel or vegetable oil. Biodiesel has the added advantage of producing less pollutant that is detrimental to the human body and also providing better lubrication to the engine body when compared to conventional diesel fuel (Bhale, January 2013). The application of biodiesel is more environmental friendly as the amount of carbon dioxide utilized by the biodiesel yielding plants exceeds the amount emitted to the atmosphere (Annamalai, 2011). (Annamalai, 2011) explain that the biodiesel engines having similar combustion characteristics as diesel, also offers adequate engine quality and performance in comparison to conventional application of diesel fuelled engines. Biodiesel is most commonly used in older vehicles in order to reduce emissions that lead to the increase in the pollution index. Biodiesel blends consist of mixtures of biodiesel with diesel at different composition. The typical industrial standard biodiesels found in the market are B2, B5, B10 and B20, which the consequent numbers to the letter B indicates the biodiesel percentage.

1.2 Problem Statement

As a major producer of palm oil, Malaysia is also greatly developing through extensive Research & Development (R&D) on the application of palm oil biodiesel products and production quality since the 1980s. It is now a growing demand in Malaysia to research and develop a new alternative for the depletion of traditional fossil fuels, in comparison with biodiesel that serves as a renewable energy. However, biodiesel is prone to react with the automotive material components, thus giving rise to engine durability and performance problems such as clogged fuel lines and filters, piston ring sticking and cocking and deposits within the system (Annamalai, 2011). (Fazal, Haseeb, & Masjuki, 2011a) states that biodiesel shows degradation in fuel quality and also corrosive reactions when in contact with different types of metal. The components of diesel fuel system that has contact with diesel or biodiesel substance are the diesel fuel, tank, fuel filter, lift pump, plunger pump, priming pump, injection pump and the injection nozzles (Bhale, January 2013).

1.3 Objectives of the study

The overall objective of the study is to understand the integrity threats to ferrous metal system components (carbon steel) carrying diesel and biodiesel fuel blends and the effect of additives or corrosion inhibitor performance to the system. This topic has been selected as a working title due to the growing demand to identify research and develop a new alternative for the depletion of traditional fossil fuels, in comparison with biodiesel that serves as a renewable. It is also essential to expand and promote the use of biodiesel within the industry in order to overcome the environmental deterioration from the effects of pollutants released by petroleum-based diesel.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Biodiesel

Biodiesel fuel has grown as a valuable alternative to the use of petroleum based fuel for many industries. Biodiesel can be defined as fuel consisting of mono-alkyl esters of long chain fatty acids obtained and processed from any natural or used feedstock that contains fatty acids. Biodiesel feedstock includes vegetable fats and oils, animal fats and also used or waste oils (Balat & Balat, 2008). The first test involving biodiesel was initiated in the early years by Rudolph Diesel, using peanut oil. The development of biodiesel has then grown steadily by research in many countries, such as France and Belgium, involving the use of other type vegetable oils and also palm oil ethyl ester. The widespread production of biodiesel (mono alkyl esters) took place in 1990s as a substitute to the growing demand of energy levels (Balat & Balat, 2008).

Biodiesels are predominantly produced from vegetable oils. The common source of biodiesel feedstock comes from coconut, rapeseed, sunflower, palm, peanut, cotton seed, soybean oil and Jathropa. Vegetable oils (triglycerides) consist of a major portion of triglycerides (98%) and small portion of mono- and diglycerides. Figure 2.1.a) shows the structure of a typical triglyceride molecule. This molecule comprises of esters from three fatty acids and one glycerol molecule. It is seen that different vegetable oils varies from one another based on the types of the fatty acid present in terms of the length of its carbon chains and the presence and numbers of double bonds within the molecule (Balat & Balat, 2008) (Ong, Mahlia, Masjuki, & Norhasyima, 2011).

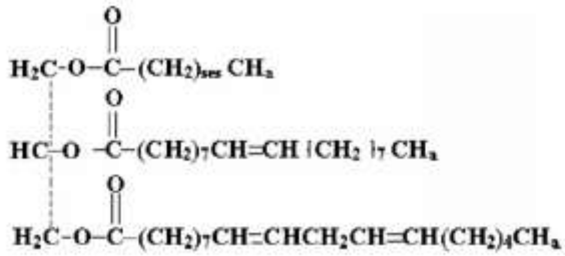


Figure 2.1 a): Chemical Structure of Triglyceride (Balat & Balat, 2008)

The feedstock of biodiesel and its production is highly depending on the availability of the feedstock in the region (Ong et al., 2011). (Ong et al., 2011) has review on the types of common biodiesel users and also its productivity. Figure 2.1 b) below shows the comparison of productivity per unit hectares for various types of vegetable oil feedstock. Based on this comparison, palm oil is seen as most potential to cater for a higher production of biodiesel. Palm oil provides the highest oil productivity when compared to other highly used feedstock in the European Union such as rapeseed oil and soybean. One of the advantages of palm oil is its continuous availability and productivity throughout the year without interruption, thus giving a higher yield when compared to other crop such as soybean and rapeseed.

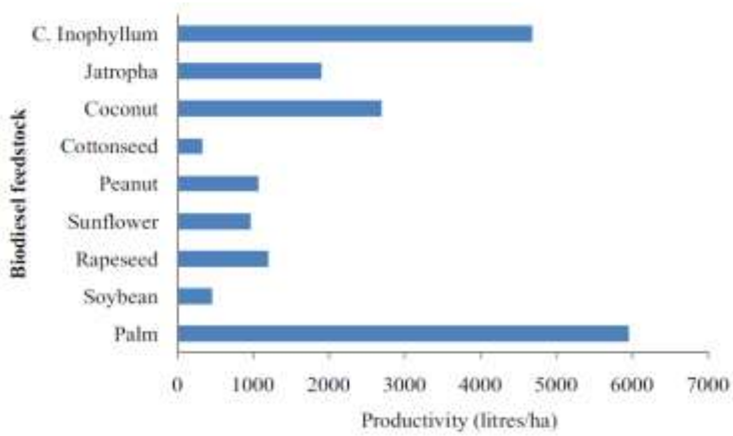


Figure 2.1 b): Production oil yield for various source of biodiesel feedstock (Ong et al., 2011)

As a major producer of palm oil, Malaysia is also greatly developing through extensive Research & Development (R&D) on the application of palm oil biodiesel products and production quality since the 1980s. South East Asia provides the highest palm oil output, which is a total of 89% from the world production. Malaysia, having 4.5 million hectares of palm oil plantation contributes to 40% of the world production (Ong et al., 2011). It is now a growing demand in Malaysia to research and develop biodiesel as a new fuel alternative that also serves as a renewable energy for the depletion of traditional petroleum fuels. In this scenario, the utilization of palm oil feedstock in biodiesel production serves as an efficient and reliable yield in terms of productivity per hectares.

2.1.1 Disadvantages of Petroleum Fuel

The production and utilization of biodiesel from vegetable oils, animal fats and waste or used cooking oil has seen to provide greater advantage in terms of environmental and also cost aspects to daily users. The main concerns involving the use of petroleum fuel involves the constant and unpredictable hike in the petroleum fuel price, which affects the need for daily use of petroleum fuel by the people. Fossil fuel is also not a renewable energy and faces depletion over time when compared to the increasing need in the fuel demand for the transportation industry. In Malaysia, crucial challenge is faced due to the increase in the final energy consumption throughout the nation. Other than that, the increase in environmental pollution and also the greenhouse effect by the use of petroleum fuel has led to serious global warning crisis. The impact of reduction in fossil fuel and environmental degradation has led to the successive research and development of biodiesel to be introduced as a much safer, cleaner and reliable alternative for fossil fuel (Balat & Balat, 2008) (Ong et al., 2011).

2.1.2 Biodiesel: Fuel for the Future

The active search for a reliable and renewable fuel has led to the drastic growth of research and development of biodiesel fuel. In comparison with all other means of alternative fuels, biodiesel based on vegetable oil feedstock has proved to be the most promising alternative with many advantages. Vegetable oils are widely available around the globe, thus making it readily available for processing and production. Vegetable oils are also renewable, whereby the source can be obtained through ongoing plantation throughout the year. Other than that, the combustion of biodiesel based from vegetable oils is also more environmental friendly, with less or no contamination such sulphur element, aromatic hydrocarbons, and crude oil residue in the source. The CO_2 emission form the combustion of biodiesel fuels is also well-balanced whereby the emitted gas is reabsorbed by the plants planted for the production of biodiesel feedstock. Biodiesel is also much safer for use and is classified as non-flammable fluid. The use of biodiesel fuels also provides better lubrication properties, thus providing better performance and life span extension for the combustion-ignition (CI) engine.

However, research has also shown that there are known disadvantages to the use of biodiesel based from vegetables oils. The use of vegetable oil has a tendency to exhibit higher viscosity that can lead to many problems in the injection and combustion process of the biodiesel. A review by (Balat & Balat, 2008) has shown that the viscosity of vegetable oil based biodiesel is 10 to 20 times greater than that using petroleum fuels. Viscosity is an essential property that affects the fuel injection equipment in the CI engine. Operating at low temperature condition also has a tendency to increase the biodiesel viscosity, leading to failures such as clogging and choking that can affect the engine performance and durability (Balat & Balat, 2008). Therefore, it is highly necessary that the viscosity properties of biodiesel to be monitored and controlled in order to improve its performance as a vehicular combustion fuel.

2.2 Biodiesel and its Properties

2.2.1 Biodiesel Production

The most common method of biodiesel production is through transesterification of vegetable oils and also animal fats. Transesterification is well-known and economical biodiesel processing method in which the vegetable oils and animals fats are reacted with alcohol such as methanol, leading to the formation of ester and glycerol. Research shows that transesterification process of biodiesel is able to lower the viscosity of the fuel and also increase combustion properties (Ong et al., 2011). The main variable affecting this process includes the type of alcohol utilized, the type and amount of catalyst, the reaction condition such as temperature and time together with the amount of free fatty acids (FFA) and water content of the origin base biodiesel. Catalytic transesterification with methanol, (methanolysis) is a common production method in which catalyst such as sodium hydroxide or sulfuric acid is used to escalate the reaction and improve the biodiesel synthesis (Balat & Balat, 2008). Figure 2.2.1 below shows the catalytic transesterification production method.

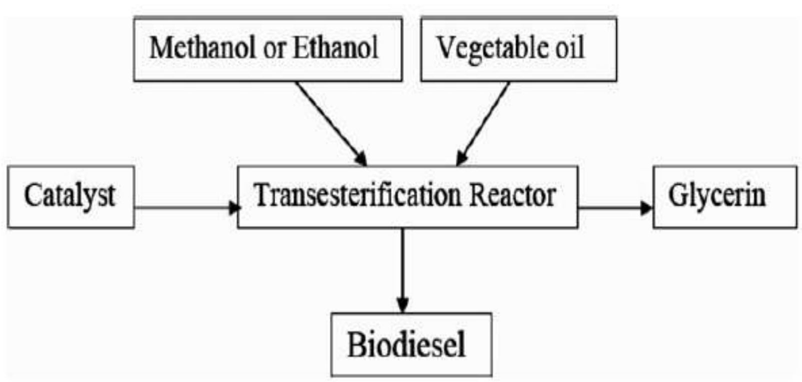


Figure 2.2.1: Catalytic transesterification production diagram (Balat & Balat, 2008)

2.2.2 Biodiesel Blends

Biodiesel is commonly used as blends with petroleum diesel. Biodiesel blends consist of mixtures of biodiesel with diesel at different composition. Biodiesel blends are indicated with the letter B and the consequent numbers to the letter B indicates the biodiesel percentage. The typical industrial standard biodiesels found in the market are B2, B5, B10 and B20. Concentration up to 5% biodiesel, B5 in conventional diesel fuel is considered to be as pure petroleum diesel. Concentrations beyond that value, which is from 6 to 20% biodiesel, can be used with little or no modification requirement for any application that currently utilizes petroleum fuel. (Tyson, September 2001) has stated that the common biodiesel blend used in the United States is B20 as it provides a well-balanced and suitable combination that is able to sustain the material selection, engine performance and cost benefits of biodiesel. Some examples of application utilising B20 are compression- ignition (CI) engines, turbines and oil boilers. (Tyson, September 2001) also reported that B20 blend has been successfully used in low-temperature climates in the US, in order to reduce the cloud point (CP) that is the temperature at which fuel starts to visually form crystals when cooled. On the other hand, biodiesel blends with higher combination such as B50 and B100 will require careful handling and also major modification to the contact equipment or process, in order to ensure the safety and compatibility of the blend to the operating system and its surroundings (Tyson, September 2001).

2.2.3 Biodiesel Properties

The property of biodiesels varies from the type of feedstock involved in the biodiesel production. (Hoekman, Broch, Robbins, Ceniceros, & Natarajan, 2012) reported that the physical and chemical properties of biodiesel are tied up to the specific composition of the fatty acid methyl esters (FAME) present in the biodiesel. A similar theory was reported by (Karmakar, Karmakar, & Mukherjee, 2010) stated that major characters such as the number of FFA and its composition in the feedstock influence the biodiesel production and final properties. FFA can be defined as the amount of fatty acid in the feedstock (wt %) that is not chemically bonded to the triglyceride molecule. Therefore, it is essential to compare the general properties of biodiesel to that of petroleum diesel, in order to achieve similar or improved performance for the automation fuel system.

Biodiesel has a higher oxygen content when compared to diesel, giving it a lower carbon and hydrogen content. This leads to a lower mass energy content in biodiesel (Hoekman et al., 2012). Biodiesel also exhibits higher fuel density when compared to diesel. The density factor is essential in the process involving fuel injector pumps and determines the energy level and air-fuel ratio within the CI engine.

In terms of cetane number, biodiesel shows an excellent value compared to diesel, in particular, No 2 diesel fuel. Cetane number represents the combustion or ignition properties of a fuel. A higher cetane number indicates a shorter delay period in ignition time and thus the fuel easily combustible. Higher speed diesel engine can operate much efficient and effectively with higher cetane number in fuels (Tyson, September 2001),(Hoekman et al., 2012). The chain length and its saturation level can influence the cetane number in a particular feedstock (Karmakar et al., 2010). Biodiesel blends tend to exhibit a higher cetane value due to the increase in B-level of the blends.

Some of the downfall in the biodiesel properties when compared to diesel properties is due to the higher viscosity of biodiesel (Balat & Balat, 2008). Viscosity represents the level of resistance in a fluid by friction within the surrounding and its fluid. A review conducted by (Hoekman et al., 2012) comparing the kinematic viscosity in 12 types of biodiesel shows that more than 80% of biodiesel exhibits a viscosity range between 4–5 mm^2/s. This comparison is also made clear by (Tyson, September 2001), proving that the higher viscosity of biodiesel when compared to diesel can be an impact to the performance and durability of the conventional CI engine. The viscosity of biodiesel is higher than that of diesel, usually by a factor of two. Higher viscosity leads to performance deterioration in terms of fuel injection volume and atomization. This problem is more significant in cold climate and low temperature operating conditions where the fuel viscosity is also highly affected by the surrounding temperature.

Cold flow peoperties of biodiesel is also one of the concern when utilizing biodiesel fuels in CI engine. Review conducted by (Bhale, January 2013) highlights that the crystallization of FAME in biodiesel at low or cold temperature can lead to clogging and choking of fuel injector pump and filters and is capable to deteriorate engine performance. The cold flow properties of biodiesel is tied to the CP and pour point (PP) of the feedstock. The CP is generally higher than the PP, which is the lowest temperature at which the fuel will crease to flow and solidify to form gel like substance (Tyson, September 2001). The CP and PP of biodiesel is generally higher when compared to diesel, typically, No 2 diesel fuel. (Bhale, January 2013) has stated that fuel selected for cold or low temperature condition is best recommended to have the lowest cold flow properties. It is seen that the low temperature flow properties of biodiesel and its higher blends is affeted by the hydrocarbon chain length and also the amount or presence of unsaturated bonds.

Another property of biodiesel that is considered under cold flow properties is the cold filter pluggin point (CFPP) (Hoekman et al., 2012). This point is defined as the the minimum temperature at which fuel form crystallization or gels and causes the filters to plug (Dwivedi & Sharma, 2014). Karmakar et. al. has reported that the CFPP of biodiesel varies according to the content of fatty acid in the feedstock, whereby the CFPP is directly proportional to the fraction of saturated fatty acid in the biodiesel. It also stated that the CFPP tends to be lower then the CP in which, upon cooling to CP temperature of the biodiesel, the methy ester molecules within the fluid tends to precipate and crystallize, leading to the clogging of fuel filters (Karmakar et al., 2010). (Dwivedi & Sharma, 2014) informed that the criticality of cold flow properties is seen especially during winter season, where decreasing temperature in the surroundings is unavoidable and prolonger over a period. Fuels with higher CFPP points will lead to faster malfunction of the vehicles during these critical times. In such scenarios, further alternative steps such as addition of additive and blending of fuels needs to be implemented to reduce the freezing points of fuels (Dwivedi & Sharma, 2014). A review by (Hoekman et al., 2012) concluded that the value of CP, PP and CFPP are interrelated to one another and thus can be used as an indication to determine or assess on the cold flow properties of the biodiesel feedstock.

Biodiesel exhibits a much higher flash point when compared to diesel, and is considered as less hazardaous in terms of flammability (Tyson, September 2001),(Hoekman et al., 2012). Flash point can be defined as the lowest temperature in which a fluid is able to evaporate and ignite in the presence of a heat source. (Hoekman et al., 2012) defines flash point as the inverse of fuel volatility, whereby biodiesel exhibits low volatility. Many research has shown that the low volatility of biodiesel can lead to poor combustion quality in diesel engines, thus affecting the performance of the CI engine (Balat & Balat, 2008),(Tyson, September 2001).

2.3 Factors that Affects the Performance and Stability of Biodiesel as Automation Fuel

The widespread use and application of biodiesel in the transportation industry is greatly expanding among the developing countries around the world. Therefore, it is highly necessary that research in understanding and classifying the properties of biodiesel be conducted in order to maximize the development of biodiesel fuel as automation fuel. A review conducted by (Jakeria, Fazal, & Haseeb, 2014) has shown that there are many factors that are able to affect the stability and quality of biodiesel used as automation fuel. These factors include oxidative stability, thermal decomposition, corrosion and contamination, wear and friction, microbial growth, combustion and emissions and also storage capabilities of biodiesel. These factors can cause the instability of biodiesel which will eventually lead to the alteration of biodiesel properties and composition. Findings by (Jakeria et al., 2014) states that based on the percentage of unsaturated fatty acid components within various biodiesel feedstock, palm and coconut biodiesel exhibits the least amount of unsaturated fatty acid, thus making them much more stable when compared to other biodiesel feedstock such as peanuts, rapeseed, soybean and sunflower.

2.3.1 Oxidation Stability

Oxidation stability is one of the main concerns in evaluating the performance of biodiesel as automation fuel. (Jakeria et al., 2014) mentioned that one of the main reasons of rapid oxidation in biodiesel is due to the level of unsaturated fatty acid components together with the higher number of carbon-carbon double and lower number of hydrogen molecules in the feedstock. This gives biodiesel much lower oxidation stability when compared to petroleum diesel leading to the formation of decomposition products such as acid, alcohol, peroxides and ester as sediments in the biodiesel. Oxidation stability can be determined by evaluating the concentration of antioxidant together with the total glycerine and fatty acid content (Bhale, January 2013). (Jakeria et al., 2014) mentioned that other factors such as light intensity, temperature, metallic traces within the biodiesel can also affect the rate of oxidation.

(Yaakob, Narayanan, Padikkaparambil, Unni K, & Akbar P, 2014) explains that there are two mechanisms in which biodiesel oxidation can take place that is auto-oxidation and photo-oxidation. Auto-oxidation is much more common in biodiesel feedstock and occurs readily when exposed to oxygen through a series of chain reactions involving initiation, propagation and termination. The UV light acts as an initiator that breakdown the compound such as peroxides, carbonyl and hydro peroxides into free radical that act as an initiator in the for subsequent auto-oxidation reaction (Yaakob et al., 2014). The level of oxidation susceptibility can affect basic properties such as cetane number, CP, PP and viscosity of the biodiesel feedstock. Beyond that, a drastic rate in the oxidation degradation of biodiesel can lead to the formation of insoluble high molecular weight polymers that can be harmful when in used in application.

2.3.2 Thermal Decomposition

Thermal decomposition or disintegration is also one of the major concerns in the application of biodiesel fuels. (Jain & Sharma, 2011) stated that temperature plays a key role in the stability of biodiesel whereby it is able to increase the rate of thermal deterioration. Thermal stability is defined as the capability of fuel to form asphaltenes when exposed to elated temperature conditions. This decomposition products are tar like resinous matter that can lead to the clogging and plugging of injector pumps and fuel filters within the internal CI engine (Jakeria et al., 2014) (Jain & Sharma, 2011). (Jakeria et al., 2014) stated that the chemical properties of biodiesel such as viscosity, density, oxidation, lubrication and corrosion can be influenced by the temperature exposure.

Biodiesel feedstock from vegetable oils consists of natural antioxidants that in general improve the stability of biodiesel. However, when exposed to high temperature condition, degradation of antioxidants takes place at a higher rate, thus making the biodiesel less stable. This condition is unsavoury especially in the application of CI engine, where high temperature condition is unavoidable (Jain & Sharma, 2011). (J.M. Nzikou, 2009) have studies the oxidative and thermal stability of biodiesel during frying, by comparing the quality of soybean oil (SO) and a blend of soybean: palm (6:4) (MO) at a temperature of 180°C for 12 hours. The results indicated that the increase in the temperature led to the formation of higher weight molecules that causes an increase in the viscosity of biodiesel for both types of feedstock. However, it is seen that SP biodiesel exhibits a higher viscosity when compared to SO biodiesel. This could be due to the lower level of anti-oxidants present in the MO biodiesel blend, leading to a higher decomposition rate of biodiesel.

(J.M. Nzikou, 2009) also reported a decrease in linoleic acid content, with an increase in polar compounds within the biodiesel for both types of feedstock as the frying temperature increase. Linoleic acid contributes to the highest percentage of polyunsaturated fatty acids in the feedstock and is more susceptible to oxidation degradation. Polar compounds on the other hand represent the oxidation products due to high temperature exposure. It was concluded that the decrease in linoleic acid content as a results of lipid oxidation, and increase in the percentage of polar compound is correlated with the increasing temperature of biodiesel, as shown in Figure 2.32 a) and Figure 2.3.2 b). Here, it is seen that a higher degradation rate is exhibited by MO feedstock when compared to SO feedstock (J.M. Nzikou, 2009). Many other research has also gained similar findings, concluding that the increase in the operating temperature affects the viscosity, peroxide and acid value within the biodiesel (Jakeria et al., 2014) (Jain & Sharma, 2011) (J.M. Nzikou, 2009). Therefore, it is highly necessary to analyse and understand the effects of temperature towards the performance and stability of biodiesel as automation fuel.

2.3.3 Storage Stability

Storage stability of biodiesel is a concern where prolonged duration of biodiesel storage can affect the primary composition of the fuel. Research has reported biodiesel is not be used as fuel after 6 months storage period due to deterioration in the biodiesel stability and may be detrimental in use (Jakeria et al., 2014). (Jakeria et al., 2014) reported that there is an increase in properties such as peroxide and acid value, density and viscosity of biodiesel with increasing storage time. The storage stability of biodiesel is affected by the level of air exposure and water content in the feedstock. (Bhale, January 2013) states that degradation rate of biodiesel stored for a prolonged time at lower temperature is much lower when compared to biodiesel stored for the same duration of time, at higher temperature. This is due to the induction period of biodiesel that decreases with the increase in temperature (Bhale, January 2013).

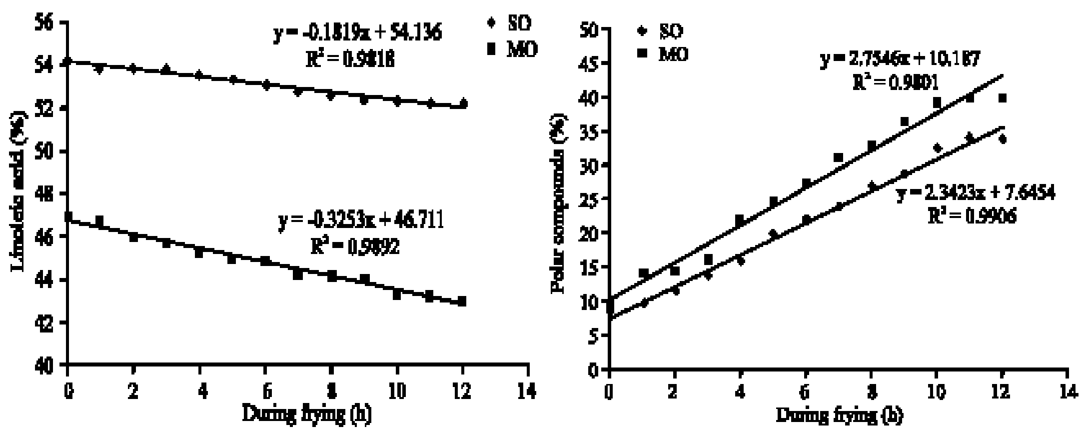


Figure 2.3.2 a): Correlation between frying hours (h) and linoleic acid content (%); **b)** : Correlation between frying hours (h) and polar compound content (%) (J.M. Nzikou, 2009)

(Bouaid, Martinez, & Aracil, 2007) researched on the effect of storage time and condition on biodiesel from vegetable oils and used frying oil after a period of 12 months. The results indicated that there is an increase in the peroxide value and acid value of all the biodiesel samples. The increase in acid and peroxide value is due to the hydrolysis of FAME to fatty acids. The viscosity of all the biodiesel blends also shows an increment with increase in storage time, whereby initial increment in viscosity only takes place when the peroxide value has reached a critical level. In conclusion, (Bouaid et al., 2007) reported that there is a significant deterioration in biodiesel fuel quality after a period of 12 months. Therefore, precautionary steps such as limiting oxygen, light and moisture excess during storage of biodiesel and also addition of additives such as antioxidants and stabilizers can improve the storage life and quality of biodiesel (Bouaid et al., 2007).

2.3.4 Corrosion and Contamination

Corrosion is one of the major deterioration faced by engine components when in contact with biodiesel. Biodiesel is seen to exhibit higher corrosive tendencies when compared to petroleum diesel due to the presence of unsaturated molecules that is prone to oxidation and decomposition (Singh, Korstad, & Sharma, 2012). The CI engine consists of main parts that come in contact with the biodiesel fuel. Figure 2.3.4 shows a typical CI diesel fuel engine system and its commonly material selection for the components. The critical parts comprises of the fuel assembly that includes fuel tank, pump, lines, filters and its injector cylinder. The level of corrosion within the CI engine depends on the type of alloy in contact with the biodiesel fuel and also the biodiesel composition such as level of unsaturation, FFA content, and also hygroscopic nature of the biodiesel (Singh et al., 2012). (Singh et al., 2012) states that corrosion is an important aspect of assessment for the widespread use of biodiesel as automation fuel as many of the components in the existing CI engine configuration consist of metal such as cast iron, stainless steel, aluminium, copper and copper alloys and also elastomers. Therefore, it is important to monitor effects of factors such as water retention, auto-oxidation, and microbial activity during storage that can lead to increase in corrosion rate of the exposed components. (Bhale, January 2013) reported that the hygroscopic nature of biodiesel that is prone to water absorption and retention can lead to increased hydrolysis of the ester chemical bonds, this forming a higher amount of FFA.

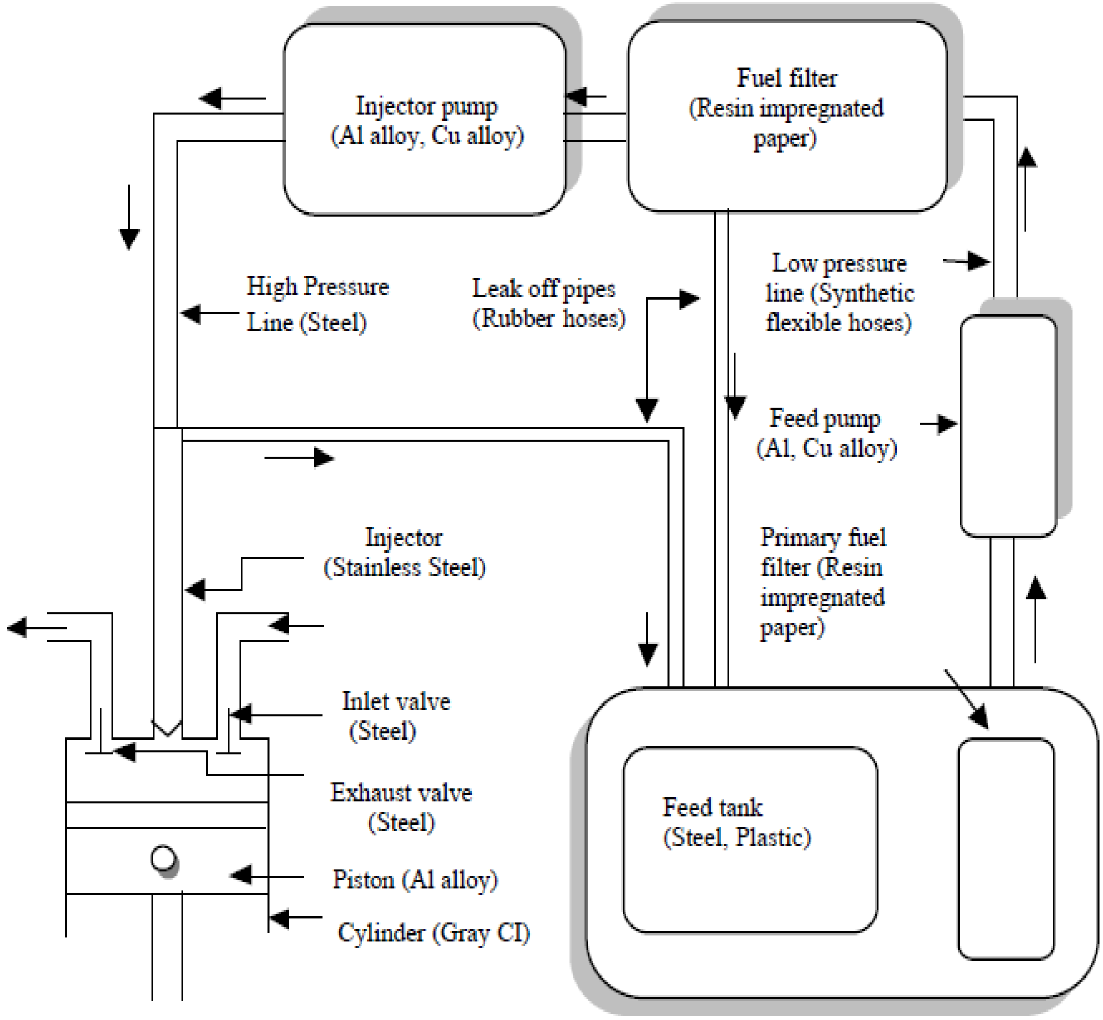


Figure 2.3.4: CI fuel engine system with common material selection (Bhale, January 2013)

2.3.5 Wear and Friction

Wear is defined as the material degradation or loss in thickness due to friction when sliding motion between two surfaces (Fazal, Haseeb, & Masjuki, 2014). The combination effect of wear and corrosion in biodiesel fuel leads to an inter-related effect and is commonly known as tribo-corrosion. The deposit formed from the action of corrosion activity over time is capable to reduce the lubrication characteristics of biodiesel at sliding points, thus increasing abrasion action, leading to engine component damage (Fazal, Haseeb, et al., 2014). It is known that biodiesel exhibits better lubricity properties when compared to diesel, however factors such as auto-oxidation, corrosion and hygroscopic nature of biodiesel, can influence the wear and friction characteristics, thus altering the chemical properties of biodiesel (Fazal, Haseeb, et al., 2014). It has been reported that biodiesel shows better lubrication and wear resistance during short term test, but it tends to lose its lubrication characteristics under long term condition, thus making it more susceptible to wear and friction (Fazal, Haseeb, et al., 2014). Therefore, it is important to study and understand the tribo-corrosion phenomena of biodiesel fuel for both long and short term condition in a typical CI engine. Engine components that are commonly affected by tribo-corrosion action are cylinder liners, pistons and piston pins and the valve assembly (Fazal, Haseeb, et al., 2014).

Many researches have shown that there is no significant change in wear characteristics when compared between biodiesel and diesel fuel (Fazal, Haseeb, et al., 2014). It is seen that biodiesel with appropriate level of FFA, monoglycerides, and polyglycerides can improve the lubrication and wear resistance properties; however, an increase beyond that level can lead to deterioration due to oxidation and corrosion (Fazal, Haseeb, et al., 2014). (Fazal, Haseeb, et al., 2014) stated that a distinct decrease of wear was seen at the range of

10–20% biodiesel. Research conducted by (Agarwal) shows that biodiesel blend B20 is capable to demonstrate physical wear reduction up to 30% lesser when compared to diesel fuel engine. Injector cocking and carbon deposit accumulation was also seen to be much lesser in the biodiesel fuelled engine. The lower increase in density of biodiesel fuel when compared to the density of diesel fuel also indicates that lesser degradation and wears contamination in the biodiesel fuel (Agarwal). Based on this research, it can be concluded that the wear and friction characteristics of biodiesel is correlated to the lubrication properties of its fuel, which is tied up to the level of unsaturated molecules and FFA content in the biodiesel feedstock (Fazal, Haseeb, et al., 2014),(Agarwal).

2.4 Economical Capability and Acceptance of Biodiesel

Biodiesel exhibits its own advantages and also disadvantages when considered to be apply as automation fuel. Certain detrimental properties such as its high viscosity and FFA content, polymerisation tendencies, moisture absorption and oxidation instability together with its high corrosive nature of biodiesel leads to the requirement for detailed and precise assessment on the short and long term durability to the CI engine prior utilization. The economy viability of biodiesel is also a factor that leads to the limitation use of biodiesel. Biodiesel is known to be more expensive than conventional petroleum diesel (Balat & Balat, 2008). (Atabani et al., 2012) mentioned that the cost of biodiesel in developing countries is 1.5 to 3 times higher when compared to the prices of petroleum diesel, thus making it less practical in terms of economy viability.

(Atabani et al., 2012) stated that costs of primary feedstock and its processing to biodiesel comprise the two main segments of cost expenditure. Similar findings were reported by (Balat & Balat, 2008) stating that 80% of the total production cost of biodiesel is allocated for the feedstock. Additional production cost is then required for the use of methanol, catalyst and labour in the biodiesel processing technology. Therefore, it was emphasised that proper selection of biodiesel feedstock is crucial in order to ensure low capital expenditure. Non-edible oils as feedstock has been recommended as a better choice in terms cost value (Atabani et al., 2012). Other than that, the production cost due to biodiesel transesterification technology can be reduced by practising continuous transesterification process, thus providing a higher production capability with reduced reaction time (Atabani et al., 2012). (Atabani et al., 2012) has also recommended biodiesel plants to have its own glycerol recovery service line, in order to ensure recovery of high quality glycerol that acts as an additional income to the main processing facility. In conclusion, more research and development emphasising on biodiesel feedstock cost, production and processing technology, properties and its effects to CI engine needs to be conducted in order to improve its economy feasibility and also to ensure the continuous growth and widespread expansion of biodiesel and it's blends as automation fuels.

2.5 Material Selection for a Typical CI Engine System

A typical CI engine system consist of three sub-assembly that is the fuel feed, combustion and the exhaust system (Haseeb, Fazal, Jahirul, & Masjuki, 2011). The basic scematic of a CI engine process flow is as shown in Figure 2.5 below. (Haseeb et al., 2011) explains that fuel flowing in the CI engine comes in contact with various types of material selected for the internal emgine components. These material can be divided into metallic and non-metallic materials that includes ferrous materials such as carbon steel, stainless steel and cast-iron together with non-ferrous material such as aluminium, copper and copper aloys. Elastomers and plactics are classified under non-metallic material.

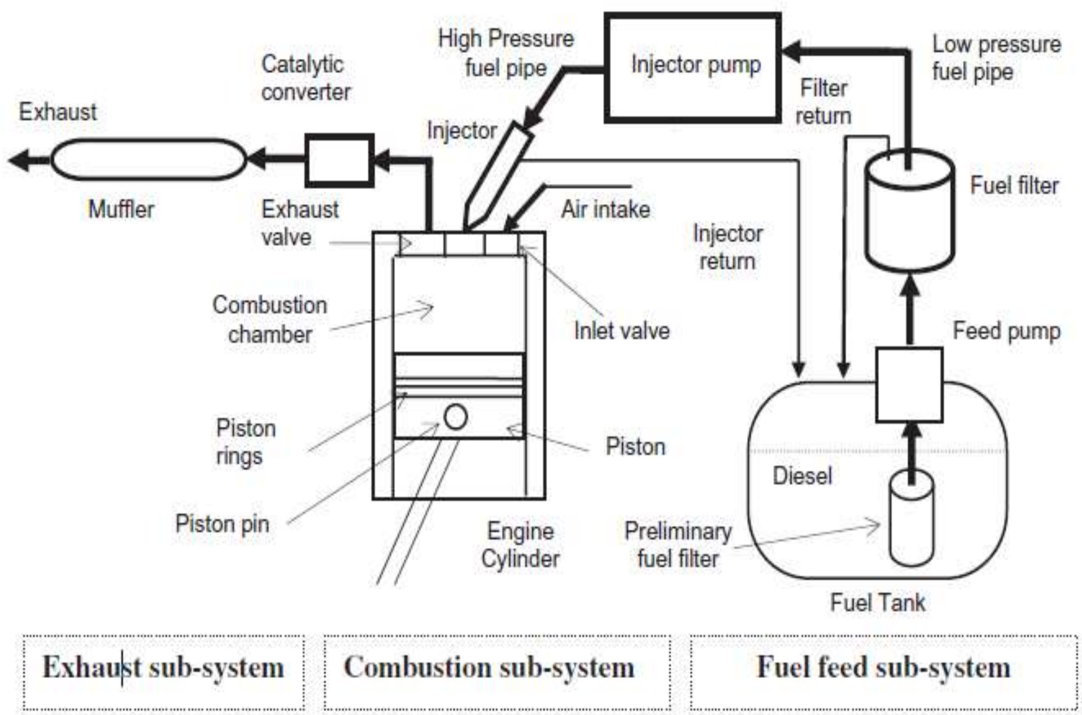


Figure 2.5: Typical process flow of CI engine (Haseeb et al., 2011)

Table 2.5 shows the common materials selected for the respestive components and systems in a CI engine. Based on the selected materials, it is seen that the fuel comes in contact with these materials at different stages and process in the CI engine and will be with different chemical properties due to the changes in the operating condition and process based on the respective sub-section (Haseeb et al., 2011). Therefore, it is important to understand the effects of biodiesel towards respective material categories in the CI engine. In general, it is seen that various materials react differently in terms of corrosive characteristics and wear degradation when in contact with biodiesel fuel. Other than that, it is also important to determine the most compatible biodiesel blends that is able give the excellent corrosion properties by reducing metal loss and preventing degardation of biodiel fuels when in contact with the respective metals.

Table 2.5: Material selection in the construction of typical CI engine components and systems (Haseeb et al., 2011)

Main parts	Components	Materials
Fuel tank	Housing	Steel, plastic, paint, coating
	Gasket	Elastomer, paper, cork, copper
Fuel feed pump		Aluminum alloy, iron based alloy, copper based alloy
Fuel lines	High pressure	Steel
	Low pressure	Plastics, rubber
Fuel filter	Filter cartridge	Paper
	Housing	Aluminum, plastic
Fuel pump		Aluminum alloy, iron based alloy, copper based alloy
Fuel injector		Stainless steel
Cylinder	Cylinder head	Gray cast iron, cast aluminum, forged aluminum
	Cylinder barrels	Gray cast iron, steel, cast aluminum
	Cylinder liner	Gray cast iron, aluminum
	Valves	Steel casting
Piston assembly	Piston	Sand-cast aluminum, die-cast aluminum, forged aluminum, gray cost iron
	Piston pin	Steel
	Piston ring	Special cast iron, steel
	Bearing	Copper alloy
	Connecting rod	Steel, aluminum alloy
Exhaust system	Exhaust manifold	Cast iron
	Exhaust pipe	Steel
	Catalytic converter	Stainless steel, ceramic fiber, aluminum fiber
	Muffler	Steel

2.6 Corrosion of Ferrous Metal in Different Biodiesel Blends

(Marta A. Jakab, 2008) conducted an experiment to test the integrity of carbon steel specimens by using standard 1 in. by 1 in. of low carbon steel (ASTM 36) immersed in two B100 biodiesel blends derived from soy oil and animal fat and two types of petroleum diesel consist of 7 ppm and 4000 ppm sulphur content respectively. The corrosion behaviour was measured through the use of an electrochemical impedance spectroscopy (EIS) whereby the samples were partially immersed in the fuel blends to measure the corrosion activity at the air/fuel interface. The impedance signal is used to measure the conductivity of cell across two electrodes, whereby one electrode acts as the reference electrode while the other acts as the working electrode. The impedance spectrum was recorded weekly for a 90-days exposure period (Marta A. Jakab, 2008). The test involves various fuel blends and combination of biodiesel and petroleum diesel.

The results upon 90-day period indicated that there was no significant corrosion activity measurement. The visual inspection indicated small traces of surface rusting due to the reaction between the surface oxide layer and the fuel blend (Marta A. Jakab, 2008). The results also indicated that the corrosion activity was more significant in carbon steel specimen immersed in animal-fat biodiesel when compared to soybean biodiesel blend. Substantially higher corrosion rate was also observed in fuel blend with 5% animal-fat biodiesel and 95% petroleum diesel with 7ppm sulphur content. This finding is as explained by (Karmakar et al., 2010) stating that animal fats and waste cooking oils contain larger amount of FFA when compared to vegetable oils, thus making the biodiesel feedstock more instable and susceptible to corrosion. It was mentioned that crude vegetable oil contains 0.3 to 0.7% of FFA content while animal fat contains 5-30% FFA content (Karmakar et al., 2010).

(J.Kaminski, 2008) experimented on the corrosion properties of carbon steel grade A765, and stainless steel grade SS 304 under the influence of microorganisms. The fuels tested includes diesel fuel (B0), Biodiesel fuel (B100) and biodiesel blends, B5, B20, B35 and B50. The finding shows that there is a significant effect with the addition of microorganism on the total acid number (TAN) of fuels with increasing biodiesel content. In other word, it is seen that the microbiological activity is highly affected by the content of FAME in the fuel whereby there is a drastic increase in the TAN number for B35, B50 and B100 biodiesel blends. It was also seen that the viscosity of the biodiesel fuel is not influenced by the addition of microorganisms to the fuels. This shows that the viscosity factor of the fuel mainly depends on the FAME content where the viscosity for fuels with and without addition of microorganism, shows an increasing trend from B 20 to B100 (J.Kaminski, 2008). The comparison is as shown in Figure 2.6 a) below.

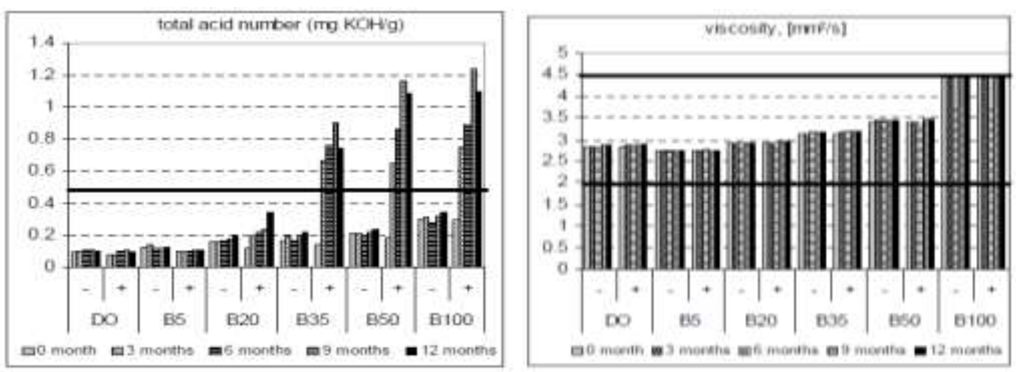


Figure 2.6 a): Comparison of TAN and viscosity of fuels with (+) and without (-) addition of microorganism (J.Kaminski, 2008)

(Maru et al., 2009) tested the corrosion behaviour of 3 different types of fuels, that is petroleum diesel with 870 ppm sulfur content (D), soybean (SB) and sunflower (SF) derived biodiesel when in contact with carbon steel and high density polyethylene (HDPE). The immersion test was carried out for a period of 60 and 115 days with carbon steel specimen and 75 and 125 days for polymer specimen. The test temperature was manintained at a temperature of 60 °C (Maru et al., 2009). The weight loss measurement after 115 days indicated that the weight reduction of carbon steel exposed to biodiesel is higher when compared to diesel. Furthermore, it is also seen that the sunflower biodiesel is much more reactive to the metal when compared to the soybean biodiesel. It was said that the difference in the corrosion activity of biodiesel feedstock is higly due to the variation in the primary chemical composition of the feedstock. This finding is agreed by (Marcos Alberto Coronado Ortega, 2013) with the statement that carbon steel is highly reactive and not compatible in the biodiesel environment.

The storage stability of soybean biodiesel in contact with carbon steel and galvanised steel has been experimented by (Fernandes et al., 2013). The experiment also measured the effects of additions, tert-butyl-hydroquinone (TBHQ) that functions as antioxidants to overcome the low oxidation stability of biodiesel. The findings indicated that the peroxide value of biodiesel in contact with carbon steel increased throughout the immersion period, but the peroxide value of galvanised steel only shown increment upon 84 days of exposure. Increasing exposure time also tends to increase the TAN in the biodiesel fuel, proving that corrosion activity increases with the formation of organic compound. Analysis on galvanised steel shows that there is a substantial amount of zinc in the diesel exposed to galvanised steel recorded since the first day of immersion (Fernandes et al., 2013). This indicates the occurrence of corrosion activity due to the presence of free-water content in the biodiesel feedstock. On the other hand, the addition of antioxidant TBHQ has shown to decrease the corrosion rate of galvanised steel with no zinc indicated in the biodiesel feedstock even after a period of 12 weeks. It was concluded that antioxidant TBHQ was being consumed in the biodiesel environment thus preserve the metal from deterioration during immersion period (Fernandes et al., 2013).

(Fazal, Haseeb, & Masjuki, 2010) experimented on the corrosion characteristics of copper, aluminium, and stainless steel in the presence of palm oil biodiesel and diesel. The testing temperature was maintained for 80°C for 600 and 1200 hours. The results, as per shown in Figure 2.6 b), indicates that the corrosion activity in stainless steel is the least when compared to aluminium and copper samples, while copper exhibits the highest corrosion rate in both diesel (B0) and palm oil biodiesel (B100). There is also no significant change in the surface morphology of the 316 stainless steel sample when observed under microscopy.

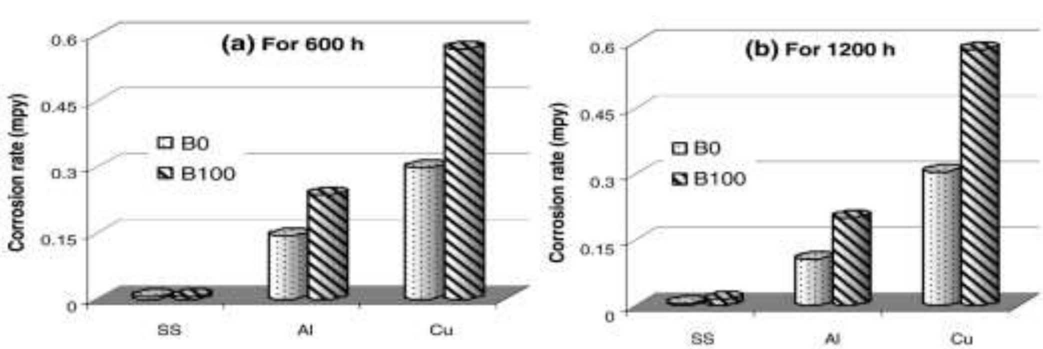


Figure 2.6 b): Corrosion rate (mpy) for SS, Al and Cu sample immersed in biodiesel (B100) and diesel (B0) for (a) 600 hours and (b) 1200 hours (Fazal et al., 2010, 2011a)

(Torsner, 2010) explains that stainless steel generates an invisible, exceedingly thin, passive film of chromium oxide that is formed on the surface of the material to protect it against the onset of corrosion and also other forms of contamination such as leaching. The protective oxide layer causes stainless steel to undergo very little leaching when compared to carbon steel. Therefore, stainless steel, namely Type 304L is very compatible in the biodiesel environment (Torsner, 2010). This statement was agreed by (Marcos Alberto Coronado Ortega, 2013) stating that stainless steel and aluminium are metallic materials that is compatible and recommended in the use with biodiesel, partly due to the formation of protective passive film on the metal surface.

Research conducted by (H.N.Meenakshi, 2010) provides assessment on the corrosion rates of carbon steel together with aluminum, copper and bronze by immersion of sample material for a period of 100h in 200 ml of biodiesel (B100), biodiesel (B99) and NaCl (1%) solution and NaCl (3%) solution individually. Figure 2.6 c) shows the corrosion rate measurement (mpy) comparison between all the 3 immersion samples for the first 24 hours. The results indicate that carbon steel shows lower corrosion rates in biodiesel when compared to that in NaCl solution. The addition of 1% NaCl was also found to increase the corrosion rate of the sample, while the highest corrosion rate was seen in the sample with NaCl medium. A commercial conductivity meter was also used to measure the conductivity of the solutions before and after exposure of carbon steel coupons. The measurements indicate that the conductivity of biodiesel blend solutions in contact with carbon steel increases after upon complete immersion period (H.N.Meenakshi, 2010).

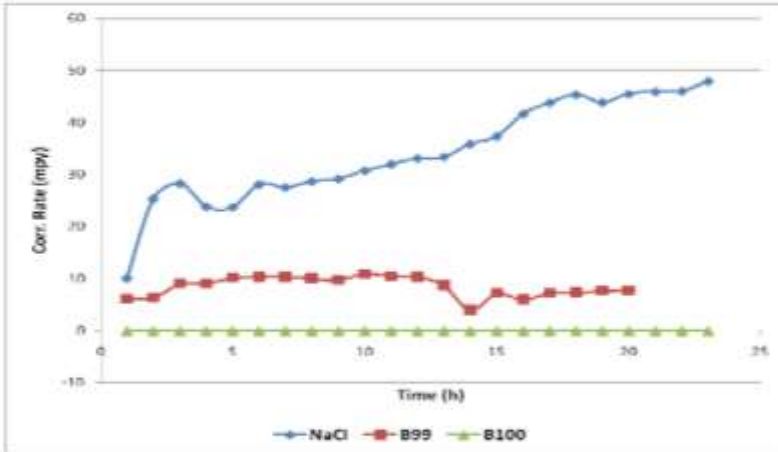


Figure 2.6 c): Deterioration trend of carbon steel as a function of time measured by LPR Method (H.N.Meenakshi, 2010)

(Fazal, Haseeb, & Masjuki, 2011c) has investigated the effect of temperature on the corrosion activity of biodiesel in contact with mild steel. The experiment was carried out at three temperatures that is room temperature, 50°C and 80°C. The mild steel samples were immersed in a solution of B0, B50 and B100 for 1200 hours, upon which the corrosion rate was calculated through weight loss measurements. The findings indicated that the corrosion rate of in each fuel increases with increasing temperature, however, biodiesel (B100) shows the highest corrosion rate followed by biodiesel blend B50 and least corrosion was seen in diesel (B0) solution (Fazal et al., 2011c).

Elemental analysis on the samples, before and after immersion also shows that there is an increase in the oxygen content with the increase in immersion temperature. The presence of oxygen was not detected on the as received sample but sample exposed to biodiesel (B100) at room temperature increases the oxygen content to 5.33 wt%, while the sample exposed to biodiesel at 80°C shows the highest content of oxygen with 10.04 wt% (Fazal et al., 2011c). It is also seen that the hygroscopic nature of biodiesel tends to increase with increasing temperature. The as-received biodiesel solution does not show any presence of water; however, there was an indication of increasing percentage of water in biodiesel solution from immersion temperature 27°C to 80°C that is 0.30% to 0.36% respectively (Fazal et al., 2011c). The increasing temperature also has the tendency to increase the oxidation rate and TAN of the sample. This finding is agreed by many research stating that the increase in temperature can increase the oxidation rate, viscosity, peroxide and acid value of the biodiesel (Jakeria et al., 2014) (Jain & Sharma, 2011),(J.M. Nzikou, 2009). It was concluded that exposure of mild steel in biodiesel leads to oxidation instability, with higher corrosion activity and is further accelerated with increasing temperature of the immersed solution (Fazal et al., 2011c).

2.7 Corrosion of Non-Ferrous Metal in Different Biodiesel Blends

Copper is one of the highly applied materials in automotive components especially for the fuel pump components. However, many published research shows that biodiesel causes enhanced corrosion activity and rapid degradation in copper base components within the CI engine (Marcos Alberto Coronado Ortega, 2013), (Fazal et al., 2010). (Fazal, Haseeb, & Masjuki, 2013) has conducted much research, investigating the behavior of copper in palm biodiesel. An experiment was carried out by immersing copper (99.9%, commercially pure) in palm biodiesel (B100) for 200, 300, 600, 1200 and 2880 h of immersion period.

The experiment results for an immersion periods of 200 to 2880 hours shows that there is an increase in the corrosion rate up to a maximum rate at 600–1200 h immersion time and decreases gradually (Fazal et al., 2013). This decrease is due to the increasing thickness of corrosion products on the copper surface, tends to decrease the area of contact for corrosion activity, thus reducing the corrosion rate of the sample. An interesting finding in this research also shows that there is a difference in the appearance of test coupons before and after exposure to biodiesel for different periods. As shown in Figure 2.7 a), the appearance if the bluish-green color is firstly seen around the edges of the sample. It is found to increases upon increase in the immersion time of the sample, which finally covers the entire surface of the sample in a strong greenish color. This is due to the conversion of copper compound on the surface of the sample, whereby the increase in the immersion time increases the thickness of the corrosion product.

The SEM micrograph results shows that there are formations of small pits randomly on the surface of the sample exposed in the biodiesel environment for 200h. The pits are also found to increase in size with the increase in immersion time (Fazal et al., 2013). Elemental analysis through EDS also shows that there is an increase in the oxygen and carbon content with the increase in immersion time of copper in biodiesel due to oxidation reactions (Fazal et al., 2013).

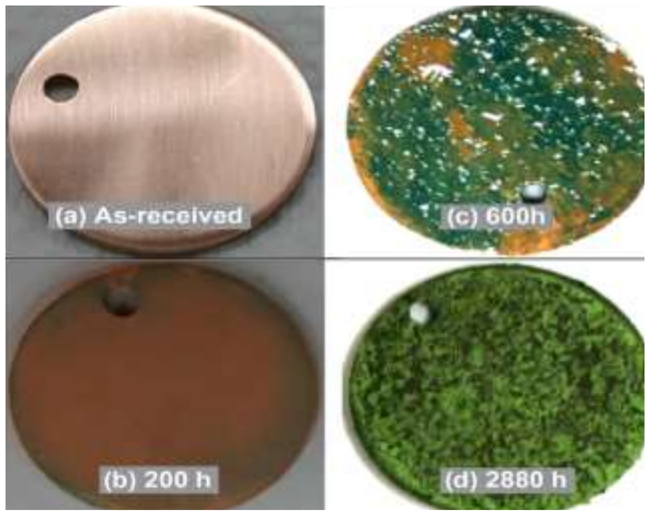


Figure 2.7 a): Deterioration trend of copper sample exposed to palm biodiesel for different immersion time (Fazal et al., 2013)

(Geller, Adams, Goodrum, & Pendergrass, 2008) supported this finding by stating that copper and copper alloys are highly reactive and more prone to degrade in the biodiesel environment. Copper and copper alloys are susceptible to pitting and also discoloration due to the formation of oxide species (Fazal et al., 2013), (Geller et al., 2008). Brass coupons show a lesser extent of corrosion rate in comparison to copper yet with similar corrosion patterns. Copper coupons in contact with 20% biodiesel solution shows a higher percentage of weight loss, that is 0.71%, while increasing biodiesel content to 80% gives a slight increment in the weight loss, that is 0.74% (Geller et al., 2008). Brass coupons are less reactive in lower concentration of biodiesels where weight loss of the samples exposed to

20% biodiesel was an average of 0.46% while those exposed to 80% biodiesel lost approximately 0.74% weight. (Geller et al., 2008) concluded that copper and /or brass components should be replaced with steel based materials as it may affect the storage, transport, quality and utilization of the biodiesel.

The performance of leaded bronze in comparison to copper in palm oil solution was investigated by (Haseeb, Masjuki, Ann, & Fazal, 2010). The experiment involves the immersion of copper (99.99% commercially pure) and leaded bronze (87% Cu, 6% Sn, 6% Pb) in three solution, B0, B50 and B100 at two different immersion temperatures that is room temperature and 60 °C. Figure 2.7 b) below shows the corrosion rate measurement, for the respective samples at different immersion temperature (Haseeb et al., 2010).

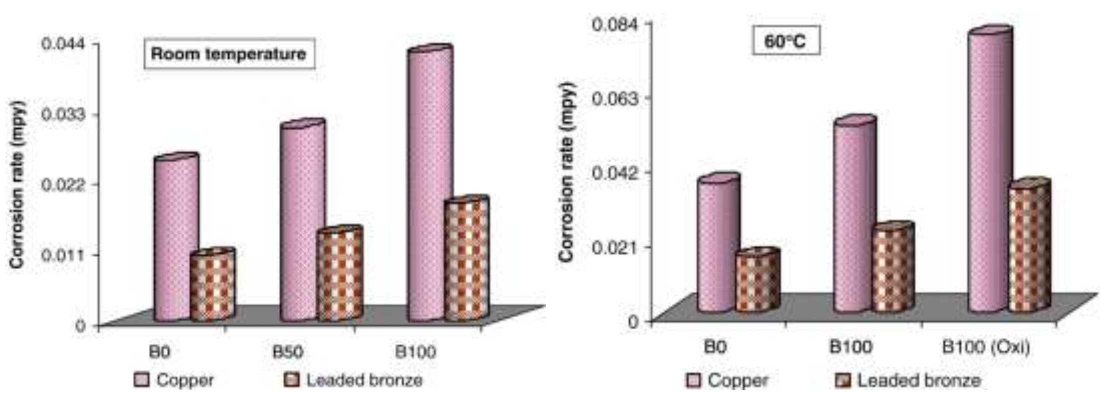


Figure 2.7 b): Corrosion rate of copper and leaded bronze at room temperature and 60°C (Haseeb et al., 2010)

Based on the above results, it is seen that the corrosion rate of copper and leaded bronze in biodiesel is higher when compared with diesel in all solutions (Haseeb et al., 2010). It is also seen that leaded bronze is less reactive and more compatible in diesel and biodiesel environment as compared to copper. Further analysis also shows that copper tends to form oxide on its surface in B100 at room temperature, while it turns into black at 60 °C. For leaded bronze, test coupons at 60 °C is cleaner and more shining compared with those tested at room temperature. The TAN assessment also shows that there is an increase in the TAN value of biodiesel upon exposure, whereby the increment is found to be similar in both copper and leaded bronze immersed solution. It was also found that the oxidation product increases with increasing biodiesel percentage in the solution (Fazal et al., 2013),(Haseeb et al., 2010).

(Sgroi, Bollito, Saracco, & Specchia, 2005) supports these findings by stating that the use of copper alloys not only causes corrosion problems but also the possibility of fuel pollutions by copper ions which may eventually affect the reagent used in the chemical reactors of the fuel processors within the CI system. Pitting corrosion was also seen in bronze filter of oil nozzles after several hours of exposure to biodiesel at 70°C. Based on these findings, it was recommended that the use of copper-free components should be emphasized especially in oil pumps and filters in contact with biodiesel environment (Sgroi et al., 2005).

Edible oils face the problem of high feedstock cost and affect the food storage, supply and demand trend when is increased in utilization as biodiesel production feedstock. Therefore, non-edible oils such as Pongamia pinnata, Calophyllum inophyllum, Madhuca indica and Jatropha curcas are widely investigated as a replacement for biodiesel feedstock (Ong et al., 2011),(Karmakar et al., 2010),(H.N.Meenakshi, 2010). (Parameswaran, Anand, & Krishnamurthy, 2013) compared the corrosion rate of copper and brass in contact with Pongamia pinnata oil (B100). It is seen that the corrosion rate of copper is much higher when compared to brass in contact with biodiesel for an immersion period of 100 hours. It was explained that brass is mainly the alloy of copper and zinc, making it more resistant to corrosion activity. The conductivity measurement of solution upon complete immersion also shows that brass exhibits lower conductance value as compared to copper. This indicates that there is a higher increase in the ionic content in copper biodiesel solution as a result of the increased corrosion activity (Parameswaran et al., 2013).

(Aquino, Hernandez, Chicoma, Pinto, & Aoki, 2012) studied the effects of natural light intensity and temperature on the corrosion activity of brass and copper samples. The experiment to evaluate the influence of light was conducted by immersing the samples for duration of 5 days in commercial biodiesel (B100) at room temperature, in the presence and absence of light. The immersion was also carried out in an oven set to 55°C, in order to simulate the condition of no light (Aquino et al., 2012). The results shows that the condition with presence or absence of light incidence at room temperature gives similar corrosion rate to both copper and brass, with a slightly higher indication of corrosion under the presence of light (Aquino et al., 2012). However, it was seen that the condition in the absence of light and higher temperature (55°C), shows a drastic decrease in the corrosion rate measured for both copper and brass sample. It was explained that the limitation to oxygen absorption and replenishment at higher temperature limits the corrosion rate activity in the immersed sample.

The optimum condition with least corrosion rate however contradicts with the optimum condition for storage stability of biodiesel. It is seen that based on the induction period and viscosity measurement, the absence of light and at room temperature is most suitable condition for the storage of biodiesel (Aquino et al., 2012). Induction period measures the duration leading to oxidative degradation of biodiesel. Figure 2.7 c) shows that the highest induction period and lowest viscosity of biodiesel is exhibited under the condition of darkness and room temperature.

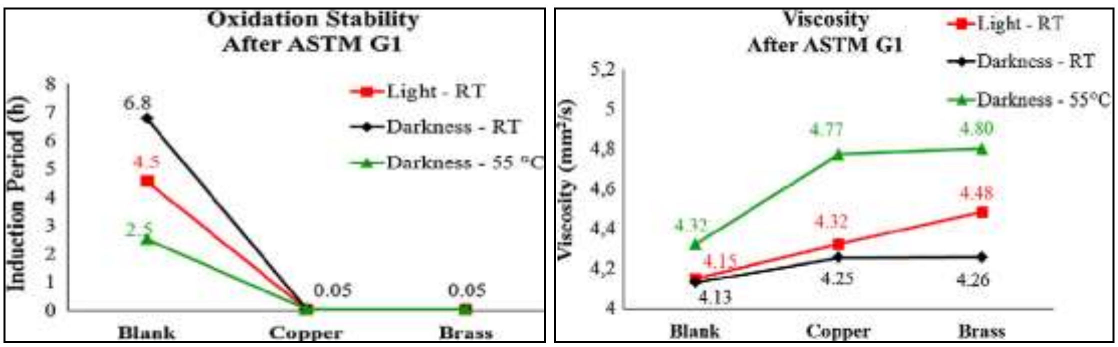


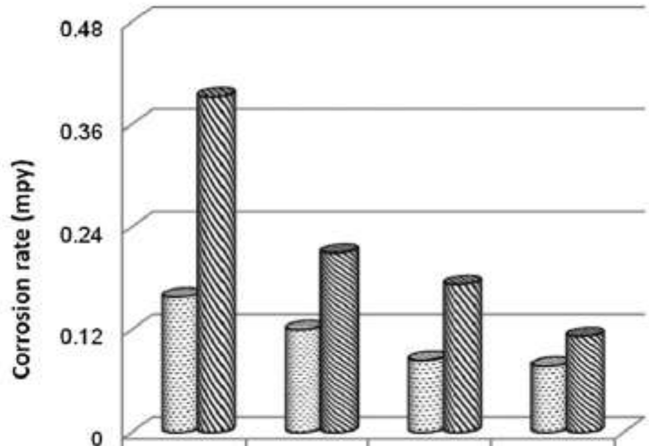
Figure 2.7 c) : Oxidation stability and viscosity measurement of copper and brass sample under various conditions of light exposure and temperature (Aquino et al., 2012)

Further study on the relationship between immersion time and fuel stability was conducted by (Fazal, Jakeria, & Haseeb, 2014) by comparing the fuel properties and palm oil composition after immersion of mild steel and copper sample for a period of 20, 40 and 60 days. The GC (gas chromatography) analysis of the fuel upon immersion shows that methyl oleate is the major constituent of palm oil biodiesel. However, it is seen that there is a drastic and continuous reduction of methy oleate in copper exposed solution, within the 20 to 60 days duration, giving a final amount of 24.62% methy oleate in the solution when compared to the initial 46.16% methy oleate before immersion. Mild steel however shows a much lesser reduction with a final amount of 42% methy oleate after 60 days of immersion (Fazal, Jakeria, et al., 2014). Methyl oleate is an unsaturated component providing oxidation sites such as double bonds that offers more reaction sites for a metal ion leading to oxidation degradation of biodiesel. It is seen that copper has a higher tendency to react with these sites when compared to mild steel, thus leading to reduction of methy oleate in the solution.

It was also seen that copper affects the instability of the biodiesel solution giving it a lower induction period when compared to mild steel biodiesel solution. (Fazal, Jakeria, et al., 2014) stated that the induction period decreases with the decrease in the methy oleate content, thus affecting the fuel properties of copper in biodiesel. Copper immersed biodiesel also shows a higher kinematic viscosity, water content and TAN of the solution when compared to mild steel immersed biodiesel. This is associated with the higher corrosion rate exhibited by copper in comparison to mild steel. The EDS analysis also shows that there is a higher content of oxygen detected on the copper sample surface than that of mild steel. This implies that there are more oxides in the copper surface, and also inside the corrosion pits. The increase in immersion time also tends to increase the oxygen content detected on the sample surface (Fazal, Jakeria, et al., 2014).

Research by (Hu, Xu, Hu, Pan, & Jiang, 2012) studies the effect of biodiesel fuel made from rapeseed oil and methanol on common automotive materials that is copper, mild carbon steel, aluminum and stainless steel. The findings are in line with other researches in the field, stating that corrosions of copper and mild carbon steel were more severe than those of aluminum and stainless steel in biodiesel. This is attributed to the reactivity and oxidation of both copper and mild steel. Minor corrosion effects were seen in aluminum and stainless steel, similar to those of diesel. This may be due to the formation of films of metal oxide, which prevents metal oxidation, thus giving lower corrosion rates. However, the corrosion rates of all four metals are still lower in diesel when compared to biodiesel environment (Hu et al., 2012). This is attributed to the higher amount of saturated fatty acids in diesel, giving it a better stability when compared to biodiesel. It was also seen that there is a higher percentage of oxygen and carbon elements on the corrosion oxide layer of biodiesel. (Hu et al., 2012) explains that the reaction between metal oxides and fatty acids of biodiesel leads to the production and adherence of reaction salts on the surface of the exposed metals. This leads to the increase in oxygen and carbon content detected on the biodiesel immersed samples.

Much research comparing the overall performance of various materials in contact to biodiesel has been conducted across the globe. This is an essential comparison as the components within a CI engine consist of both ferrous and non-ferrous metals, with different corrosion reaction and stability towards biodiesel. A study by (Fazal, Haseeb, et al., 2014) comprises on the comparison of corrosion deterioration and oxidation stability of common automotive component materials such as aluminum, copper and stainless steel, brass and cast iron in both petroleum diesel and palm biodiesel. Figure 2.7 d) supports the findings that aluminum is the most compatible material among the non-ferrous materials showing the least difference in corrosion rates between diesel (B0) and biodiesel (B100) environment. The decomposition of biodiesel produces copper and iron ions that tend to further activate various other chemical reactions (Fazal, Haseeb, et al., 2014).



	Cu	BS	Al	CI
B0	0.158296	0.120122	0.084055	0.077402
B100	0.39278	0.209898	0.173055	0.112232

Figure 2.7 d): Corrosion rate of copper (Cu), brass (BS) aluminum (Al) and cast iron (CI) in palm biodiesel (Fazal, Haseeb, et al., 2014)

(Cursaru, Brănoiu, Ramadan, & Miculescu, 2014) experimented on the corrosion behaviors of aluminum, copper and mild carbon steel exposed to sunflower biodiesel (B100), biodiesel blend (B20) and conventional petroleum diesel (B0) after static immersion tests in B0, B20 and B100 at room temperature and 60◦C for 3000 h. It is noted that the increase in temperature increase the corrosion rate. This can be attributed to the TAN factor. High TAN factor in biodiesel is due to the formation of free fatty acid in the solution. The experimental research indicates that increase in the immersion temperature, causes the TAN factor to increase in the biodiesel and consequently, the oxidation of metal in the biodiesel environment increases (Cursaru et al., 2014). The increase in temperature leads to higher oxygen content and moisture adsorption which eventually gives a higher corrosion rate. The SEM observation indicates the formation of pits on the surface of copper and mild steel upon exposure to biodiesel at room temperature and intensifies at exposure of 60◦C. Figure 2.7 e) below shows the experimental results indicating that the corrosion activity increase from aluminum to mild carbon steel to copper. The corrosion rate of all metals shows similar observation in regards of lower corrosion rate in diesel when compared to biodiesel. As seen in various research, copper tends to exhibit higher corrosion rate when compared to other materials under the same condition (Geller et al., 2008),(Haseeb et al., 2010),(Fazal, Haseeb, et al., 2014).

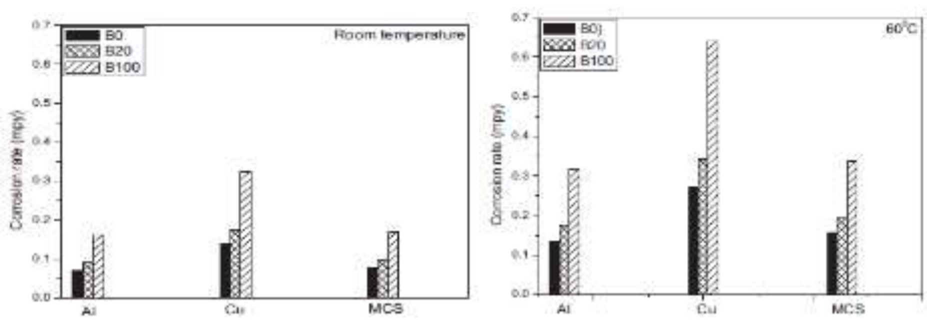


Figure 2.7 e): Corrosion rate for aluminum (Al), copper (Cu) and mild carbon steel (MCS) at room temperature and at 60 °C (Cursaru et al., 2014)

The present research studies the behaviors of copper based alloy phosphorus bronze in the presence of biodiesel and its blends. However, significant and published research on this scope is not available yet.

2.8 Additives and its Effects on Biodiesel Blends

Many research has shown that the compatibility of biodiesel to the selected materials, namely ferrous and non-ferrous materials within a conventional CI engine is still very much poor in performance when compared to diesel fuel. Therefore, it is highly necessary to develop an alternative method in order to improve the performance and quality of biodiesel as a suitable replacement for diesel fuel in the automation industry. The addition of additives is one of the alternatives that is able to improve the properties and stability of fuel (Rashedul et al., 2014). (Rashedul et al., 2014) stated that there is a vast selection of additives can be added according to improve specific limits and enhance the properties of automotive biodiesel. Commonly used additives can be further divided in terms of the purpose of its addition.

One of the major drawbacks in the use of biodiesel is the deterioration of oxidation stability of the fuel. (Bhale, January 2013) mentions that oxidation of biodiesel cannot be completely eliminated but can be reduced by the addition of antioxidants. Antioxidants are one of the common additives that functions to inhibit the oxidation process of biodiesel fuel by intercepting the formation of free radicals, thus, preventing the initiation of oxidation chain reaction (Jakeria et al., 2014). (Rashedul et al., 2014) mentioned that oxidation process leads to the formation of free radical and peroxides within the fuels. The addition of antioxidants tends to decompose the peroxide formed and acts as free radical traps to retard the biodiesel fuel oxidation process. Antioxidants are also used to improve the flash point and cetane number of the biodiesel fuel properties (Rashedul et al., 2014).

(Almeida et al., 2011) researched on the effects antioxidant tert-butyl hydroquinone (TBHQ) towards the storage stability of biodiesel. The storage stability of biodiesel with and without the addition of antioxidant was evaluated through static immersion test with copper corrosion coupons (Almeida et al., 2011). The result shows that the addition of antioxidant TBHQ shows higher induction time for the biodiesel fuel of 24 hours during initial exposure condition. The oxidation stability of biodiesel without the addition of TBHQ antioxidant shows a period of 6.5 hours. However, both samples shows similar oxidation trend with prolonged exposure to pro-oxidative condition, giving an approximate induction period of 2.42 hours after 24 hours. This trend is as shown in Figure 2.8 a) (A) below proving that antioxidant did not improve the oxidant stability of biodiesel under prolonged exposure to similar condition. On the other hand, Figure 2.8 a) (B) shows that the copper concentration measurement shows a higher amount of copper residue formed in the solution without the addition of antioxidant TBHQ when compared to the solution in the presence of TBHQ. This shows that the presence of antioxidants retards the corrosion process, by protecting the coupon surface from corrosion activation sites (Almeida et al., 2011).

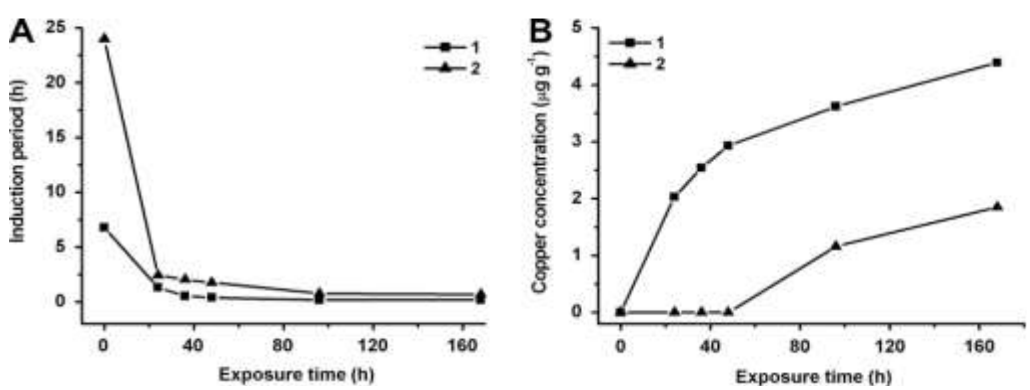


Figure 2.8 a): (A) Induction period measurement for biodiesel (1) without and (2) with TBHQ antioxidant addition. (B) copper concentration for biodiesel (1) without and (2) with TBHQ antioxidant addition (Almeida et al., 2011).

Corrosion inhibitors are also considered as effective additives to improve the corrosion reactivity of biodiesel when in contact with CI engine components. (Fazal, Haseeb, & Masjuki, 2011b) defined the corrosion protection mechanism in which corrosion inhibitors leads to the formation of an enduring, resistive layer on the metal surface, thus reducing contact point at the metal/solution interface. It has been reported that amine based compounds such as primary amines, diamines, aminoamines, and oxyalkylated amines are effective corrosion inhibitors in diesel. (Fazal et al., 2011b) has investigated the performance of three common corrosion inhibitors, ethylenediamine (EDA), n-butylamine (nBA), tert-butylamine (TBA) of cast iron in contact with palm oil biodiesel. The results of corrosion rate calculation shows that all three addition of corrosion inhibitor is able to reduce the corrosion of cast iron, when compared to corrosion rate of cast iron in biodiesel without corrosion inhibitor additive. The effectiveness of corrosion inhibitor is as shown in Figure 2.8 b), with decreasing performance from EDA>TBA>nBA (Fazal et al., 2011b).

However, further analysis on fuel samples shows that the fuel properties of biodiesel with EDA addition undergoes greater degradation when compared to fuels with addition of other corrosion inhibitors. Based on this assessment, it was found that TBA is most effective in reducing corrosion activity whereby the formation of protective layer iron nitrite hydrate, prevents oxygen or water contact on the metal surface, thus eliminating the formation and dissolution of metal oxides. In comparison of fuel TAN and density, TBA added biodiesel shows an optimum performance due to the lower amount of corrosion products and sediments formation (Fazal et al., 2011b).

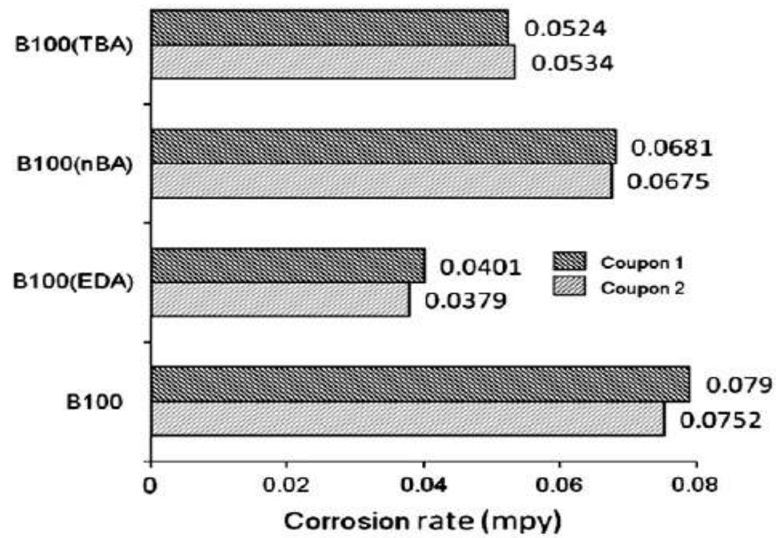


Figure 2.8 b): Corrosion rate of cast iron in the presence of palm oil biodiesel with and without addition of corrosion inhibitor (Fazal et al., 2011b)

Benzotriazole (BTA) is a well-known corrosion inhibitor used to inhibit corrosion activity of metals, especially of copper and its alloys (Allam, Nazeer, & Ashour, 2009). The chemical structure of BTA consist of benzene and triazole rings, $C_6H_5N_3$. (Allam et al., 2009) explains that the structure of BTA with free electrons enables itself to bond on the copper surface, thus preventing the occurrence of corrosion. Many researches has been conducted to understand the effects of BTA in copper and its alloys exposed to various condition and environments such as strongly acidic, alkaline and neutral solutions. It was stated that the performance of BTA is most effective in clean environments, whereby the presence of pollutants such as sulfide ions, is able to not only retard the performance of BTA against corrosion of copper and its alloys but also increase the corrosion rate to a greater level leading to faster metal degradation (Allam et al., 2009).

A review by (Finšgar & Milošev, 2010) on the inhibition of copper corrosion by addition of BTA mentions that a protective barrier film, mainly composed of copper and BTA complex, is formed as the copper surface is penetrated by BTA. This mechanism prevents the discoloration and staining of copper surface. (E. Guilminot, 2000) studied the performance of BTA as corrosion inhibitor of archaeological polished copper and archaeological copper covered with corrosion products exposed to aqueous polyethylene glycol (PEG). The result shows that the addition of BTA was less significant for polished copper samples, whereby the presence of PEG was sufficient to limit the dissolution current of the polished copper sample. On the other hand, samples covered with corrosion products were highly affected by PEG, whereby corrosion products degradation increases with time. Here, the presence of BTA was able to reduce the dissolution current of the corrosion product, thus protecting the corrosion layer of the copper. It was seen that the higher protection was achieved with increasing BTA concentration and immersion time (E. Guilminot, 2000).

(Khan, Shanthi, Babu, Muralidharan, & Barik, 2015) studied the effect of BTA of various concentration and velocity towards providing corrosion protection to copper samples. The samples were immersed in 3.5% NaCl test solution with and without the presence of BTA at different concentrations and velocities. The result as shown in Figure 2.8 c) proves that BTA provides sufficient protection to the copper sample, whereby increasing BTA concentration in the solution reduces the weight loss of the sample. It was also seen that increasing the velocity of the sample rotation increases the weight loss of the sample. (Lei, Sheng, Hyono, Ueda, & Ohtsuka, 2014) investigated the effects of BTA addition to the formation of Polypyrrole film (PPy) on copper for corrosion protection purposes. The corrosion inhibitor was added into the oxalic acid aqueous solution that consists of pyrrole monomer. The results of the experiment indicated that the addition of BTA in the solution caused the initial formation of BTA-Cu complex layer followed by the anodic polymerisation of PPy layers. Analysis on the copper sample showed that the adhesion of PPy film was more homogeneous and stronger due to the presence of BTA-Cu complex layer on the copper surface, that support to coordinate the systematic adhesion of the PPy monomers. (Lei et al., 2014) also explained that the presence of the BTA-Cu film acts as a second barrier that supports to inhibit corrosion activity if the PPy layer was damaged locally. It was also seen that the presence of BTA in the oxalic acid solution reduces the corrosion effects to the copper sample. The dissolution of cipper immersed in 3.5wt % NaCl for 480h was retarded with 80% inhibition efficiency when compared to bare copper (Lei et al., 2014).

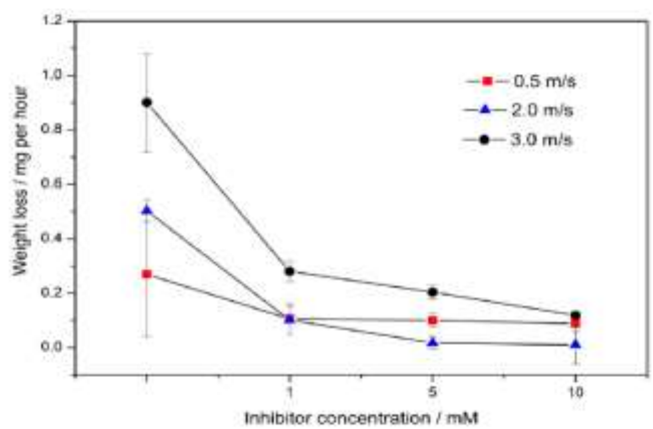


Figure 2.8 c): Effects of BTA concentration and sample rotating velocity to the weight loss of copper sample (Khan et al., 2015)

(Kosec, Milošev, & Pihlar, 2007) studied the effects of BTA addition as corrosion inhibitors for brass in chloride solution. The tested samples includes copper, zinc and copper-zinc alloy, Cu-10Zn and Cu-40Zn. It was seen that the addition of BTA decreases the corrosion current for all metals tested, however, highest inhibition efficiency was seen in sample Cu-10Zn. It was explained that the higher inhibition efficiency of the sample was due to the formation of copper based alloy having a better resistance in chloride containing solution. It was concluded that BTA is an effective corrosion inhibitor for zinc metal as well. The formation of a mixed copper-zinc protective oxide surface acts as an effective barrier for both metal components in the copper alloy.

2.9 Summary

Conclusion drawn by (Ravichandran, Nanjundan, & Rajendran, 2004) stating that TBA and BTA derivative corrosion inhibitors are excellent additions for improving corrosion protection. In summary, biodiesel has a promising potential to be a reliable and renewable fuel replacing petrol diesel fuel in the future. With continues research and support, suitable and improve material will be able to withstand the highly corrosive process of the biodiesel blends and producing the same results when comparing the performance with petrol diesel.

CHAPTER 3

MATERIALS & METHODS

This chapter gives a full list of chemicals and reagents to be used in conducting the research. The brand of the chemicals and reagents used are also given alongside the materials. Also under this chapter, brief explanations of the synthesis procedure and characterization steps taken are also given.

3.1 Material

3.1.1 Low Carbon Steel S45C

1m length of low carbon steel S45C sample was purchased from a local company. The samples were cut to a size of 22.0 mm in diameter and 2.0 mm thickness. It comes with 1 x 2mm holes that were drilled near the edge of each specimen to hanging it into the immersion solution. The cross section of the sample is shown in Figure 3.1 below.

Figure 3.1: Low Carbon Steel S45C

The chemical compositions of low carbon steel S45C are shown in Table 3.1.1

Table 3.1.1: Chemical compositions of low carbon steel S45C

Chemical	Compositions
Carbon (C)	0.42% - 0.48%
Silicon (Si)	0.15% - 0.35%
Manganese (Mn)	0.6% - 0.9%
Phosphorus (P)	0.03% max
Sulphur (S)	0.035% max

3.1.2 Biodiesel

The commercial biodiesel used in this research was purchased from Weschem Technologies Sdn. Bhd. in Batang Kali, Selangor. Biodiesel is used in this research as the target solution to study the corrosion trend and behavior of the test sample. Biodiesel is used in its pure form, B100. The parameters for B100 fuel are specified through the biodiesel standard, ASTM D6751. This standard identifies the parameters that pure biodiesel (B100) must meet before being used as a pure fuel or being blended with petro diesel. B100 also is used to produce biodiesel blends of B20 and B50. The properties of the commercial biodiesel are as shown in Table 3.1.2.

Table 3.1.2: Properties of Commercial Biodiesel

Section: BIOFUELS
Specification for Biodiesel (B100)

Property	ASTM Method	Limits	Units
Calcium and Magnesium, combined	EN 14538	5 max.	ppm
Flash Point	D93	93.0	Degrees C
Alcohol Control (one of the following must be met)			
1. Methanol Content	EN 14110	0.2 max	% mass
2. Flash Point	D93	130 min	Degrees C
Water & Sediment	D2709	0.050 max	% vol
Kinematic Viscosity, 40°C	D445	1.9 - 6.0	mm^2/sec
Sulfated Ash	D874	0.020 max	% mass
Sulfur S15 Grade	D5453	0.0015 max	% mass (ppm)
Sulfur S500 Grade	D5453	0.05 max	% mass (ppm)
Copper Strip Corrosion	D130	No. 3 max	
Cetane Number	D613	47 min	
Cloud Point	D2500	Report to customer	Degrees C
Carbon Residue 100% sample[a]	D4530	0.050 max	% mass
Acid Number	D664	0.50 max	mg KOH/gm
Free Glycerin	D6584	0.020 max	% mass
Total Glycerin	D6584	0.240 max	% mass
Phosphorus Content	D 4951	0.001 max	% mass
Distillation, T90 AET	D 1160	360 max	Degrees C
Sodium/Potassium, combined	EN 14538	5 max	ppm
Oxidation Stability	EN 14112	3 min	hours
Cold Soak Filterability	Annex to D6751	360 max	seconds
For use in temperatures below -12 C	Annex to D6751	200 max	seconds

3.1.3 Diesel

The commercial diesel used in this research was purchased from Petron Malaysia. Diesel was used in its pure form, B0 and also in biodiesel blends, B20 and B50. The properties of the commercial diesel are as shown in Table 3.1.3 below.

Table 3.1.3: Properties of Commercial Diesel

Properties	Value
Density at 15 ºC (kg/l)	0.8296
Kinematic Viscosity at 40 ºC (cSt)	3.400
Flash Point (ºC)	62
Sulfur content (ppm)	358
Ester Content (%)	0.0

3.1.4 Tert-Butylamine (TBA)

TBA is one of the four isomeric amines of butane. This chemical compound is used as an effective corrosion inhibitor (CI) in the diesel environment. The chemical for this research was purchased from R & M Chemicals in Semenyih, Selangor. It is commercially available in a colorless liquid form, with a strong amine odor. The properties of TBA are as shown in Table 3.1.4 below.

Table 3.1.4: Properties of TBA

Properties	Value
Molecular Formula	$C_4H_{11}N$
Molecular Weight (g/mol)	73.14
Melting Point (ºC)	-67.50
Boiling Point (ºC)	43 - 47

3.1.5 Benzotriazole (BTA)

BTA is a heterocyclic compound commonly used as CI in the presence of copper and its alloys. BTA for this research was purchased from a local company where it was produced by Alfa Aesar. It is commercially available in a white to light tan, crystalline powder form. The properties of BTA are as shown in Table 3.1.5 below.

Table 3.1.5: Properties of BTA

Properties	Value
Molecular Formula	$C_6H_5N_3$
Molecular Weight (g/mol)	119.12
Melting Point (ºC)	100
Boiling Point (ºC)	350

3.2 Equipment

3.2.1 Metallography Grinding & Polishing Machine

This machine is used to grind the low carbon steel S45C test sample prior to immersion testing. This step is essential in order to remove the scratches and oxide layer present on the sample. These layers need to be removed in order to ensure the accuracy of the weight loss and corrosion rate measurement of the low carbon steel S45C sample. The silicon carbide grinding paper grade goes from 800 to 1200.

3.2.2 Analytical Balance

This machine is used to measure smaller masses in sub-milligram scale, such as the weight of low carbon steel S45C sample, before and after immersion testing together with the weight of chemicals and additives added to the solution. The equipment is shielded in a transparent enclosure, also known as draft shield with doors to prevent the collection of dust, contaminants and air current to affect the accuracy of the measurements and its deviance.

3.2.3 Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX)

This machine is used to analyze the image of the low carbon steel sample upon complete immersion and also to study the elemental composition or chemical characterization of the sample. The model of the equipment is Hitachi SU1510 SEM & Horiba EMAX EDX. The SEM analysis was carried out at a magnification of 3000X. The similar sample was then subjected for EDX analysis.

3.2.4 Acid Value Tester

This machine is used to determination of the free fatty acid content of animal and vegetable oils and fats. The model of the machine is G20 Compact Titrator by Mettler Toledo It quantifies the amount of potassium hydroxide (KOH) in milligrams that is needed to neutralize one gram of the test solution. The testing takes place by titration of the test solution with KOH solution, which is a strong basic solution. The result determines the amount of KOH utilized in the neutralization process thus indicating the level of acidity in the test solution.

3.2.5 Density Meter

This tester is used to determine the density of the test solution. This is a portable density meter that is lightweight and suitable for on-site measurement. The model of the tester is DMA 35 by Anton-Paar. The density is measured in units g/cm^3 @15 ºC.

3.3 Methodology

3.3.1 Sample Preparation

The low carbon steel S45C sample was abraded with 800, 1000 and 1200-grit silicon carbide papers in order to remove scratches and oxide layer present on the sample. Samples were then washed by deionized water and degreased with acetone. The initial weight measurement of low carbon steel S45C sample was measured prior to immersion using an analytical balance that come with four decimal points accuracy.

The first set of immersion solution consist of pure biodiesel, pure diesel and biodiesel blends. Biodiesel blends are indicated with the letter B and the consequent numbers to the letter B indicates the biodiesel percentage. In this experiment, the biodiesel blends refers to B20 and B50 solution. B0 represents pure diesel solution, while B100 represents pure biodiesel solution. B20 and B50 on the other hand consist of 20:80 and 50:50 ratio of biodiesel-diesel solution respectively. The biodiesel blend solutions were prepared by measuring the specific amount of biodiesel and diesel required to form a 500ml solution. The specific amount for biodiesel blend immersion solution is as shown in Table 3.3.1.

The second set of immersion solution was experimented with the addition of CI in biodiesel blends, B20 and B100. Chemical TBA and BTA have been added in the immersion solution based on the respective calculation required for a 500ml immersion solution.

Table 3.3.1: Biodiesel Blend Components

Beaker Numbering	Biodiesel Blend	Components		Total (ml)
		Biodiesel (ml)	Diesel (ml)	
1	B0	0	500	500
2	B20	100	400	500
3	B50	250	250	500
4	B100	500	0	500

3.3.2 Immersion of Test Sample

The low carbon steel S45C test samples that has been labelled and weight for initial weight measurement is then tied to thin bamboo sticks using a tie string. The tie is secured with sellotape to ensure that the test sample is always in a vertically upright position, while being immersed completely in the solution in the beaker. The setup involves three low carbon steel S45C test samples tied in a horizontal line, in a single stick and fitted into the immersion solution beaker. This is necessary to obtain a more precise and accurate average in the weight loss of test sample upon complete immersion period. The beaker is then tightly closed with shrink wrap material to prevent contamination and moisture from the environment from affecting the immersion test process. The experimental setup is as shown in Figure 3.3.2.

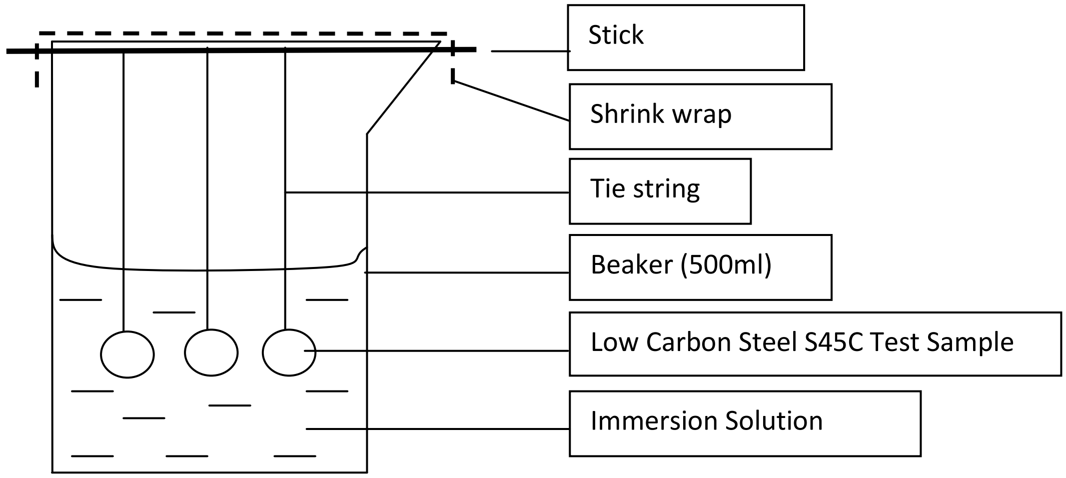


Figure 3.3.2: Experimental setup for immersion of Low Carbon Steel S45C test samples

The similar setup was produced for the remaining immersion solution, giving a total of eight experimental trials tested on 24 low carbon steel S45C test sample. The samples have been immersed for a period of 1440 hours. The experimental setup was stored at room temperature, approximately 25ºC to 27 ºC and relative humidity, approximately 82%.

3.3.3 Weight Loss Measurement

Upon completion of immersion test, the samples were cleaned carefully by using a polymer brash in order to remove the corrosion products. The sample was dried under a blower and the weight of each sample after immersion test was recorded by using an analytical balance to four decimal points accuracy. The weight loss measurement is applied to determine the corrosion rate of the test sample. Corrosion rate measurement determines the analytical measurement and extent of corrosion on the low carbon steel S45C samples. The obtained data from weight loss will be converted into corrosion rate (mpy) by using Eq. 1 below;

$$\text{Corrosion rate (mpy)} = \frac{W \times 534}{D \times T \times A} \qquad (1)$$

where corrosion rate in units 'mpy' stands for mils (0.001 in.) per year, W is the weight loss (mg), D is the density (g/cm3), A is the exposed surface area (square inch) and T is the exposure time (h). The effects on addition of additives or corrosion inhibitor are determined by comparing the corrosion rate of sample with and without addition to obtain the percentage of corrosion inhibitor effectiveness.

3.3.4 Characterization Study

The characterization study of test sample and immersion solution was carried out upon complete immersion testing. The characterization study can be divided into metal and fuel characterization test.

3.3.4.1 Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX)

The low carbon steel S45C test sample was subjected to SEM and EDX at Quasi-S Sdn. Bhd, UKM-MTDC Smart Technology Center, Universiti Kebangsaan Malaysia. The test samples were stored in an air-tight container prior testing. Each sample was tested for SEM and EDX at three different locations on the sample, in order to obtain an average result when analyzing the sample image and elemental composition.

3.3.4.2 Total Acid Number (TAN)

The test solution was measured up to 10g in a 250 ml flat bottom flask using an analytical balance. The test solution was then mixed with 80mL Ethanol 95% reagent solution. The flask was fixed to the acid value tester and the testing was initiated. The titration of the free fatty acids in the solution of potassium hydroxide takes place, and the amount of KOH solution used in the neutralization process is recorded. The final result indicates the total amount of KOH required to neutralize the test solution. A higher TAN value indicates more acidic test solution, with higher number of free fatty acid.

3.3.4.3 Density

The filling tube is connected to the density meter. The pump level on the density meter is pressed down and held, while the filling tube is submerged in the test solution. The pump level is then slowly released, as the test solution is drawn into the density meter. The density measurement appears on the meter screen and is recorded.

CHAPTER 4

RESULTS AND DISCUSSIONS

This chapter gives full results of the experimental from the methods described in Chapter 3 with complete explanations.

4.1 Corrosion Rate

Figure 4.1.1 shows the corrosion rate of low carbon steel S45C upon exposure to different biodiesel blends without the presence of different corrosion inhibitors. Results show that corrosion rate is increased proportionally with the increasing of biodiesel blends. It reveals that biodiesel is comparatively more corrosive than pure diesel used in this research when low carbon steel S45C is taken as a subject material.

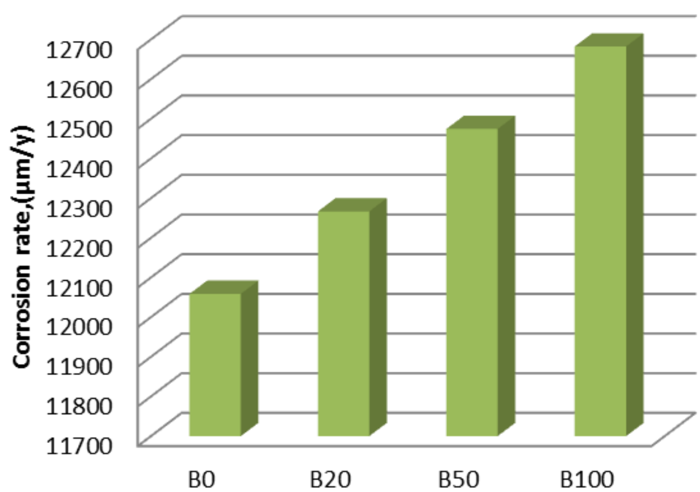


Figure 4.1.1: Corrosion rate of low carbon steel S45C sample in different biodiesel blends without corrosion inhibitor

Figure 4.1.2 shows the corrosion rate of low carbon steel S45C sample in B20 and B100 biodiesel blends with the presence of corrosion inhibitor, TBA and BTA. The corrosion rate of low carbon steel S45C in B20 and B100 biodiesel blends with the presence of corrosion inhibitor is found to be further reduced with the addition of corrosion inhibitors, as also reported by (Fazal et al., 2011b). TBA shows significant impact as most effective corrosion inhibitor in the present condition when compared to BTA although both inhibitors technically effective in reducing corrosion rates of low carbon steel S45C in different biodiesel blends.

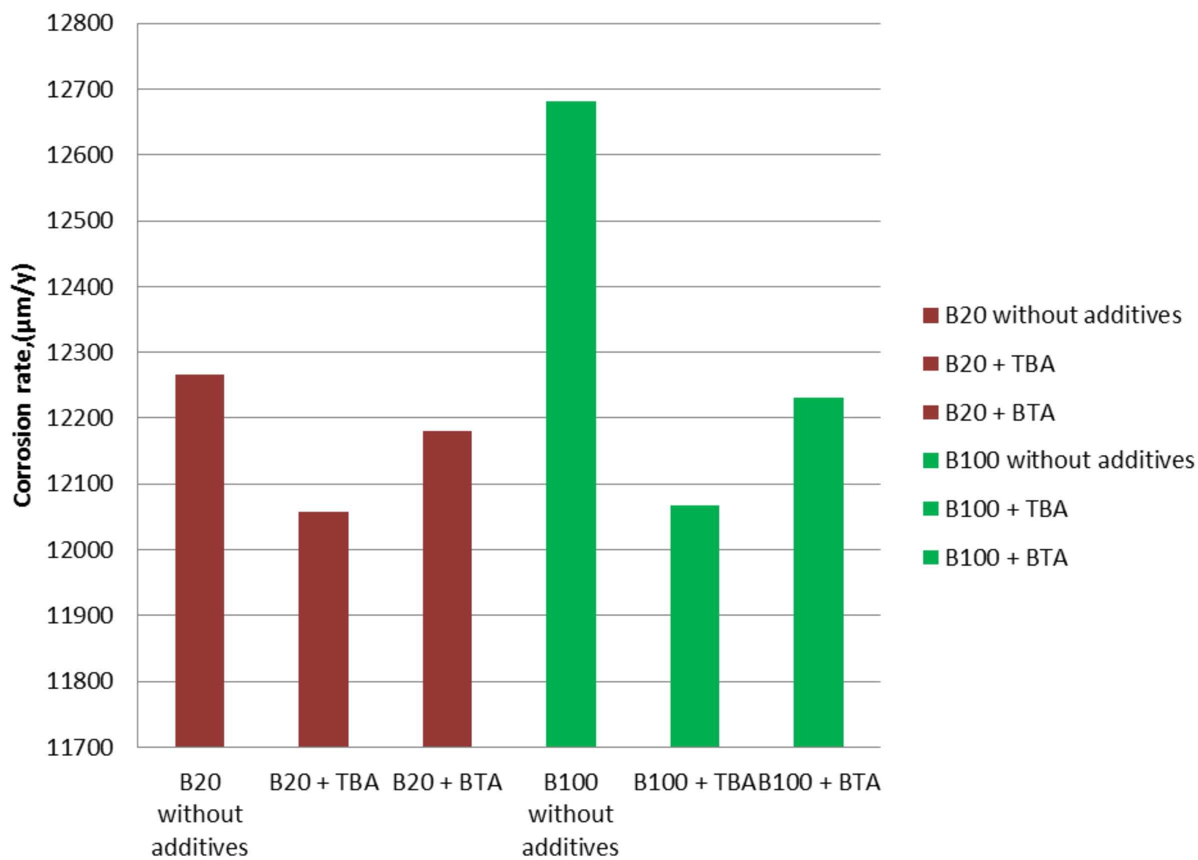


Figure 4.1.2: Corrosion rate of low carbon steel S45C sample in B20 and B100 blends with the presence of corrosion inhibitor, TBA and BTA

4.2 Visual Inspection on the samples

The physical image of the low carbon steel, LCS S45C samples at the end of the corrosion test was recorded using digital photography (Figure 4.2.1). The photographs show different images of corroded metal surface in different types of biodiesel blends, without the presence of corrosion inhibitors. The images support the corrosion rate results shown in Figure. 4.1.1. More corroded metal surface is recorded throughout the increasing blends between the pure diesel solutions and biodiesel.

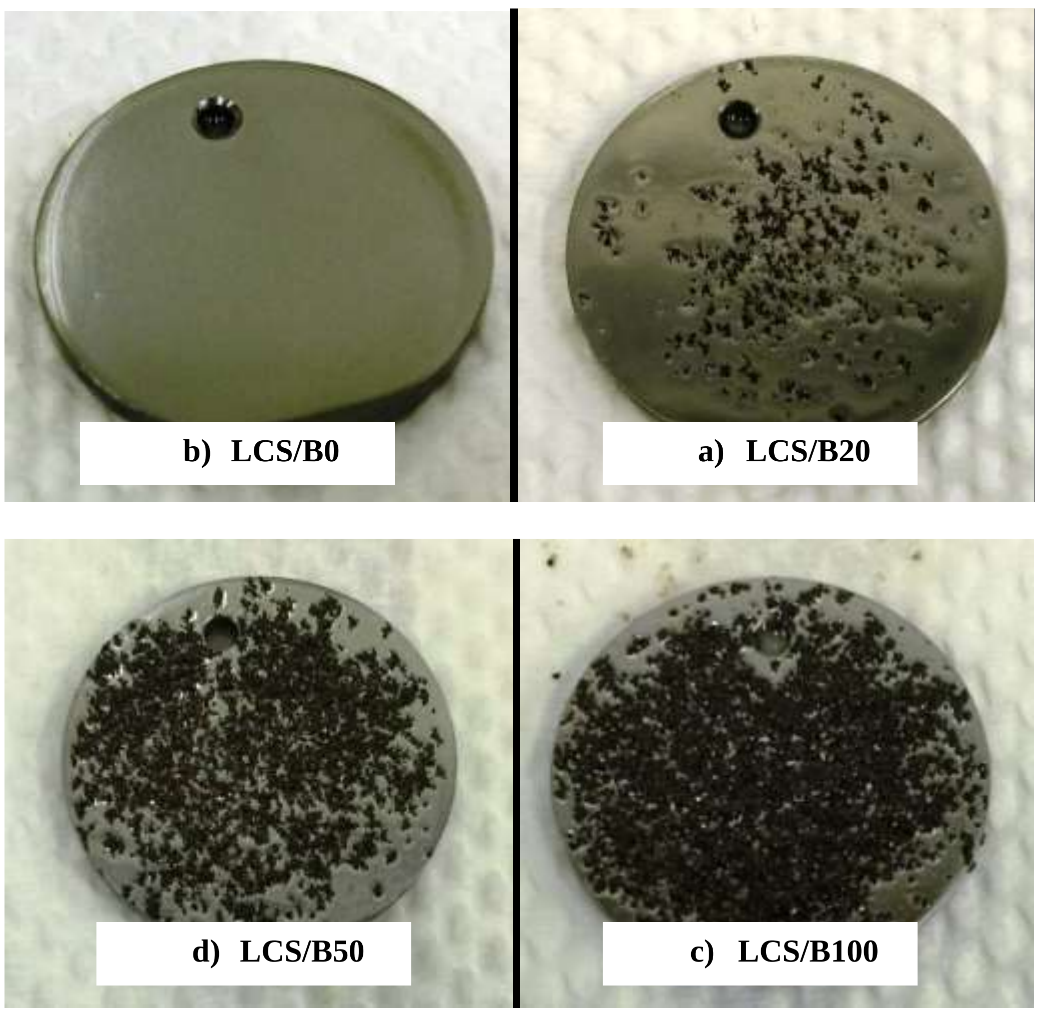


Figure 4.2.1: Photograph of low carbon steel S45C sample without corrosion inhibitors at the end of corrosion test

Physical image of the low carbon steel S45C samples in B20 and B100 biodiesel blends with the presence of corrosion inhibitors, TBA and BTA at the end of the corrosion test was recorded in Figure. 4.2.2 and Figure. 4.2.3 below.

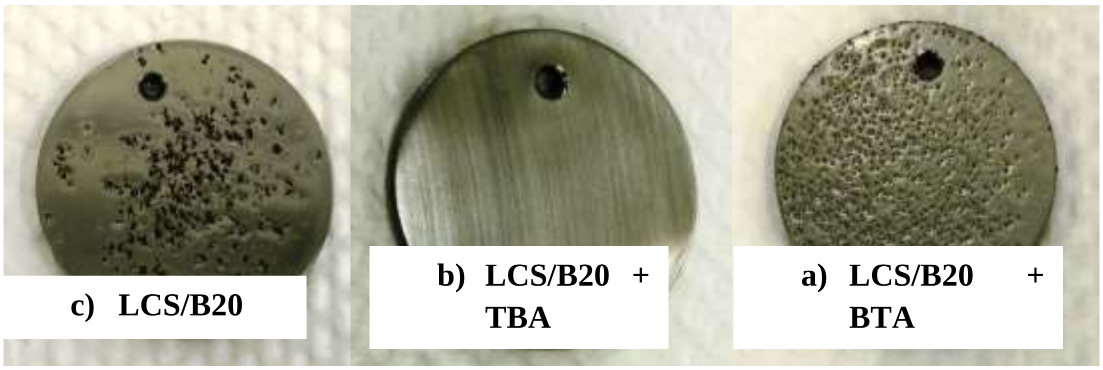


Figure 4.2.2: Photograph of low carbon steel S45C sample in B20 biodiesel blends with corrosion inhibitors at the end of corrosion test

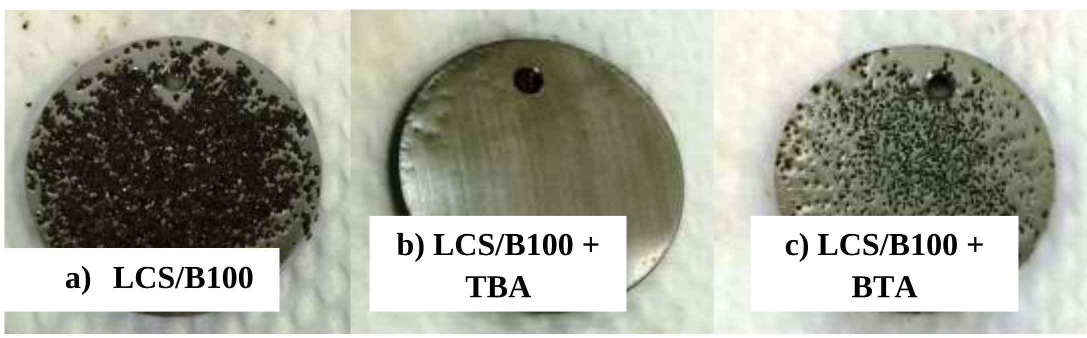


Figure 4.2.3: Photograph of low carbon steel S45C sample in B100 biodiesel blends with corrosion inhibitors at the end of corrosion test

It is observed that corrosion attack on biodiesel exposed surface is comparatively higher than that of inhibitor added biodiesel. Figure 4.2.2 and Figure 4.2.3 display that inhibitors TBA containing biodiesel exposed sample is cleaner with almost no sign of corrosion rate happen physically when compared to inhibitors BTA containing biodiesel exposed samples.

4.3 Scanning Electron Microscope (SEM)

Further investigation of surface damage are done with all samples were cleaned in same procedure and the image were then taken using scanning electron micrographs as shown in Figure 4.3.1 and Figure 4.3.2.

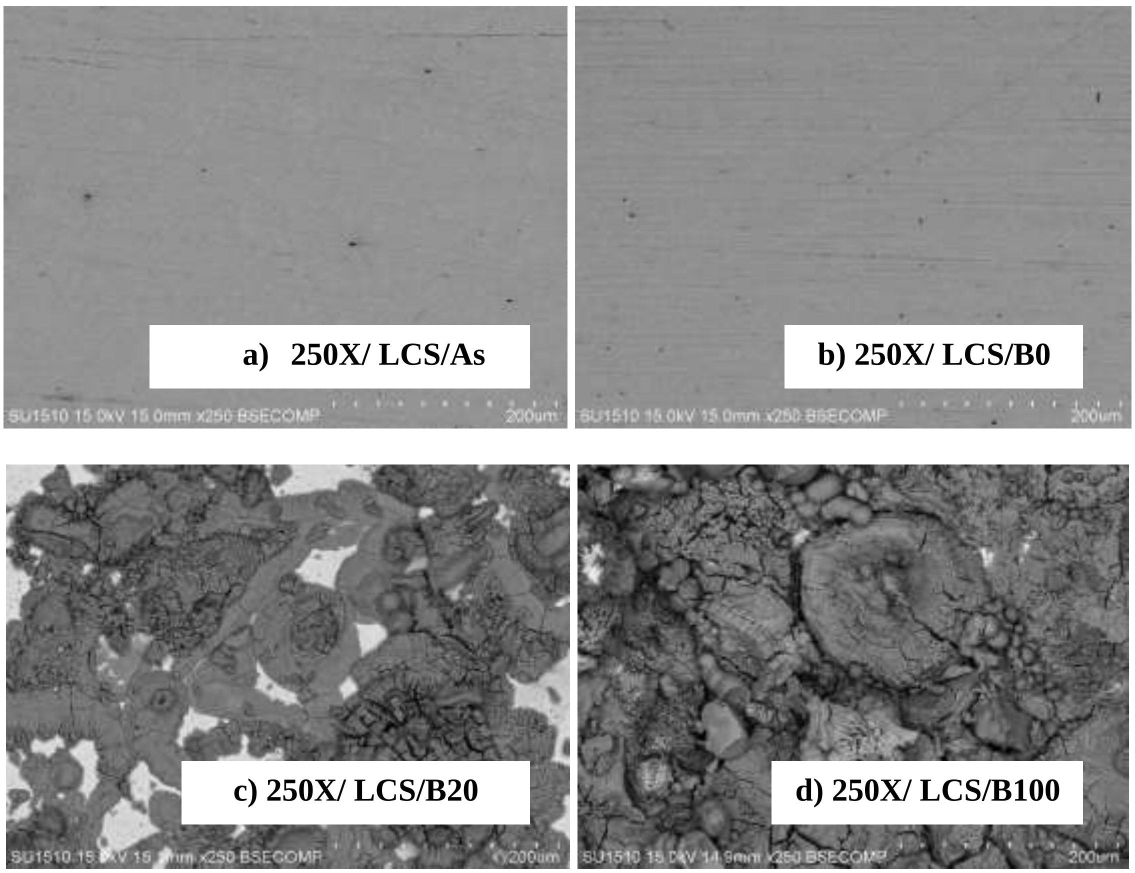


Figure 4.3.1: SEM micrographs of low carbon steel S45C surfaces when exposed to different biodiesel blends without the presence of corrosion inhibitors.

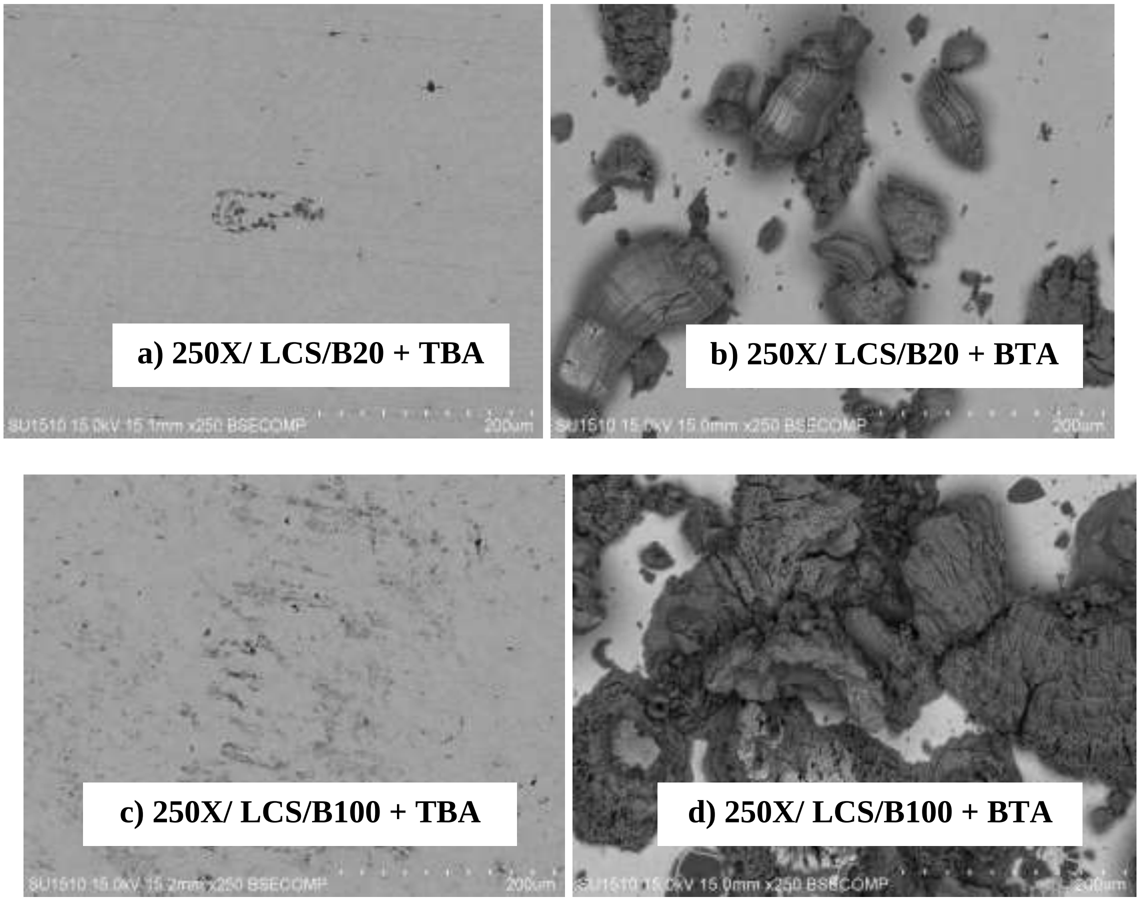
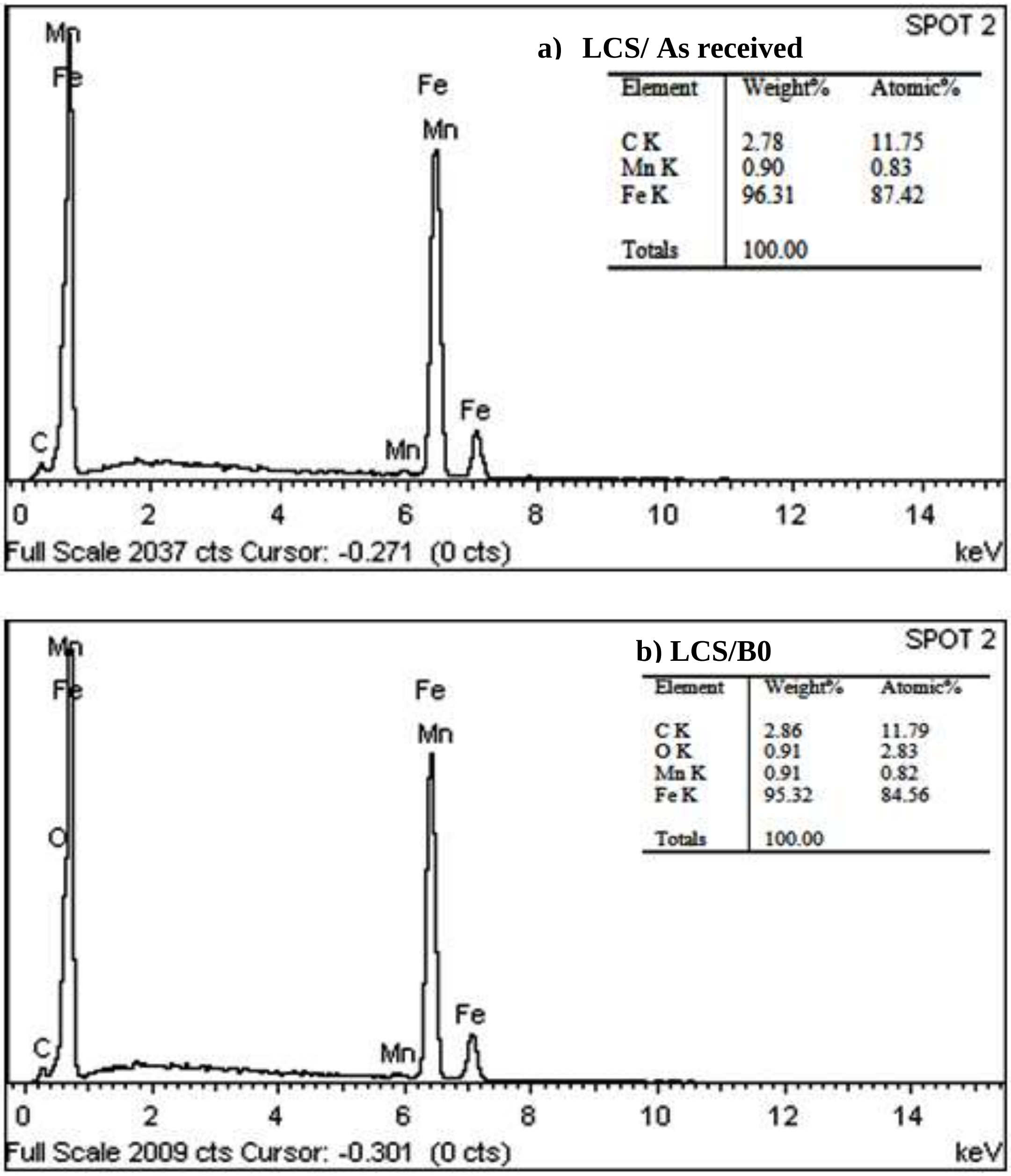


Figure 4.3.2: SEM micrographs of low carbon steel S45C surfaces when exposed to B20 and B100 biodiesel blends with the presence of corrosion inhibitors.

Photographs of post corroded sample show the corrosion product on the surface upon addition of different corrosion inhibitors except for TBA. SEM micrographs show relatively higher corrosion attack on higher blends of biodiesel exposed surface than others. Less corrosion attack was found for the sample exposed to TBA added corrosion inhibitors.

4.4 Energy Dispersive X-Ray (EDX)

EDX study was performed to investigate the corrosion inhibitors added biodiesel exposed surface. EDX pattern taken on the corroded surface of low carbon steel S45C are shown in Figure 4.4.1.



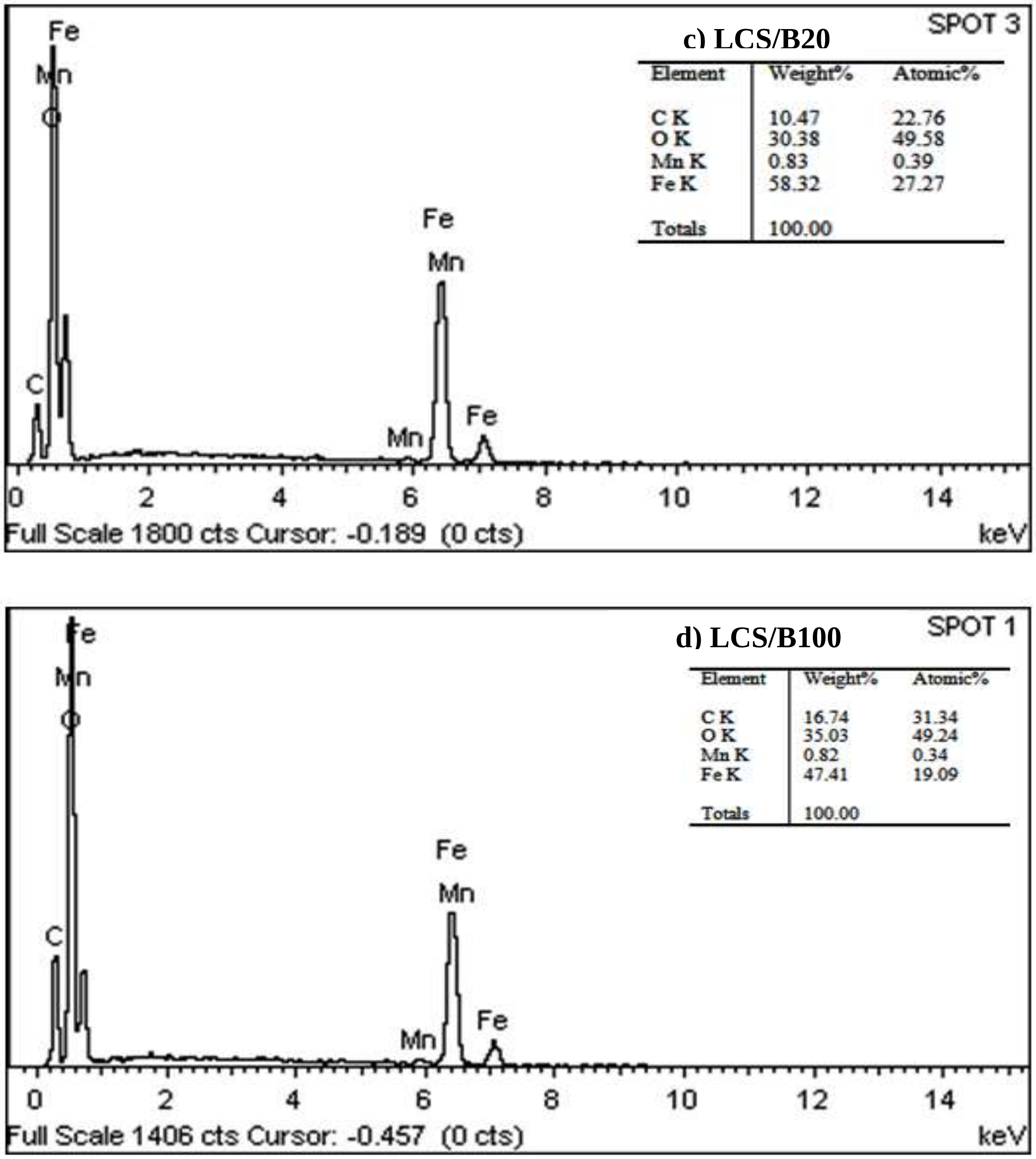
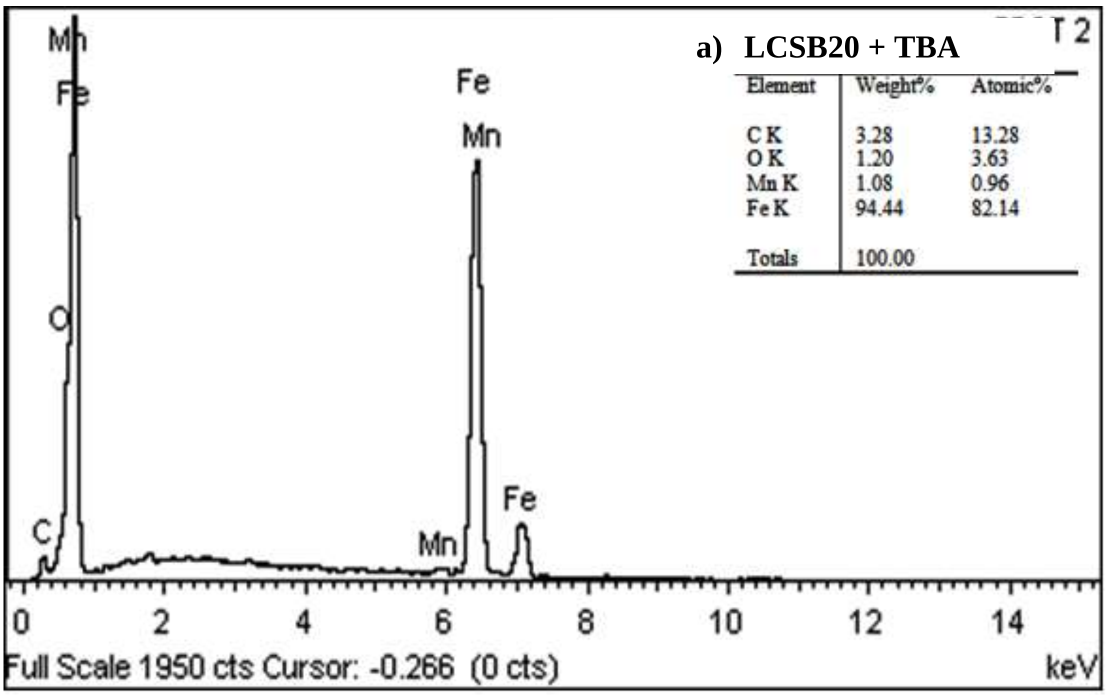


Figure 4.4.1: EDX of low carbon steel S45C sample without the presence of corrosion inhibitors

The elemental study was conducted on samples immersed in diesel solution and also B20, B50 and B100 solution, with and without additive addition. Figure 4.4.1 shows the elemental study of low carbon steel S45C in the respective condition, without additive addition. Based on the evaluation done, it is seen that there is increasing oxygen content on the sample surface, with increasing biodiesel content in the immersion solution. The as-received sample does not indicate any elements of oxygen on the metal surface. Sample immersed in pure diesel solution, B0, contains the least amount of oxygen, while sample immersed in pure biodiesel solution contains the most amount of oxygen content.



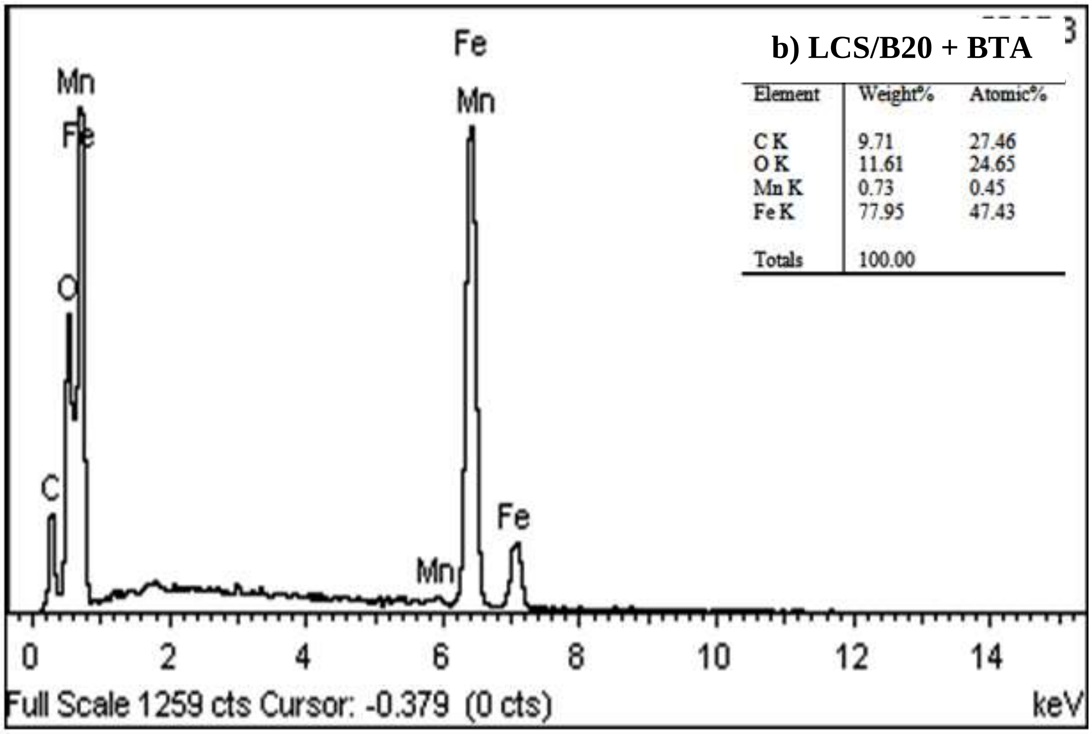
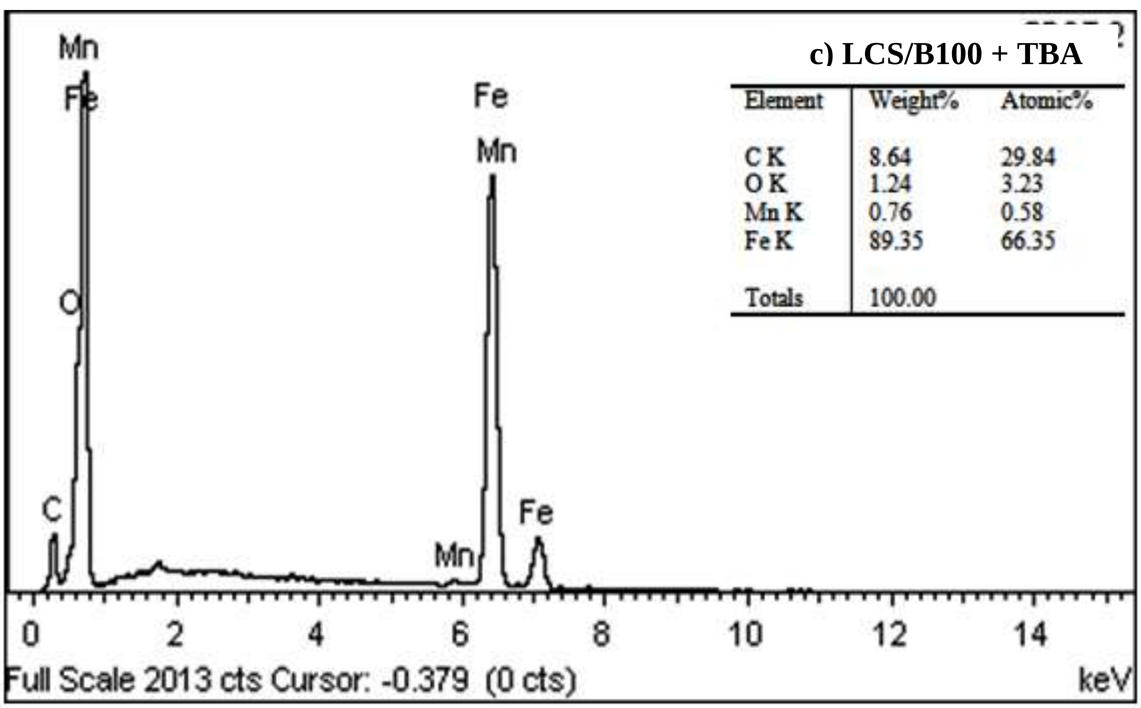


Figure 4.4.2: EDX of low carbon steel S45C sample in B20 solution with the presence of corrosion inhibitors



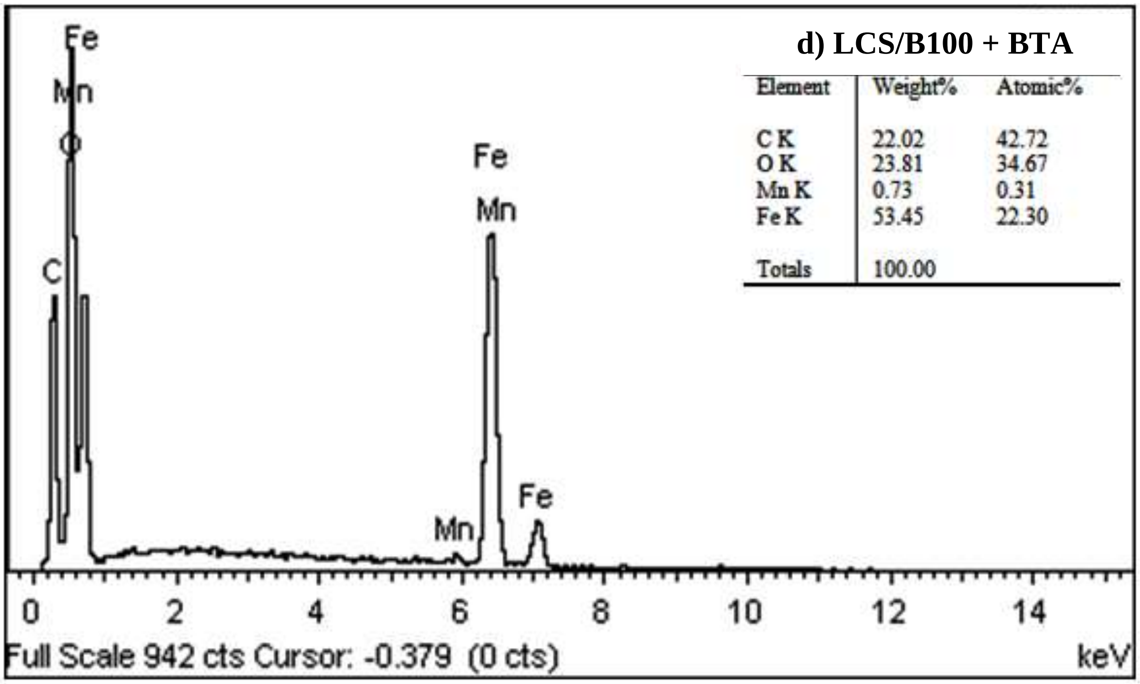


Figure 4.4.3: EDX of low carbon steel S45C sample in B100 solution with the presence of corrosion inhibitors

The comparison of elemental analysis between sample B20 and B100, without corrosion inhibitors and sample B20 and B100, with corrosion inhibitors shows that the corrosion inhibitor works in favors to retard the corrosion activity on the metal surface. In Figure 4.4.2and Figure 4.4.3 shows the elemental study of low carbon steel S45C sample in the respective condition, with the presence of corrosion inhibitors. A similar trend was seen where both results showing that TBA respectively are a better characteristic of preventing corrosion from happen when compared to BTA. Based on the EDX results, there is a decrease in the oxygen content accordingly from 30.38 wt % in B20 solution to 1.2 wt% in B20 solution with TBA addition to finally 11.61 wt% in B20 solution with BTA addition. The iron, Fe content on the other hand shows an increasing trend, with 58.32 wt% in B20 solution, 94.44 wt% in B20 solution with TBA addition and 77.95 wt% in B20 solution with BTA addition. The similar trend was seen when comparing the elemental analysis in

B100 solution and also B100 solution with the presence of TBA and BTA corrosion inhibitors respectively.

(Fazal et al., 2011b) mention that amine based corrosion inhibitor such as TBA seems to reduce the subsequent metal oxide formation and dissolution by forming stable oxide layer on metal surfaces. According to (P. Li, 1997), amine based inhibitors protect corrosion primarily through its adsorption onto the metal surface. It also state that adsorption can occur through metal-nitrogen atom bonding via π-electrons by chemisorption or with a protonated amine through the formation of a hydrogen bond to the metal surface. (Yıldırım & Çetin, 2008) reported that adsorption of the molecules over the metal surface via O atoms present in their ester functional groups realized with weaker interactions than adsorption of heterocyclic moiety via N atom. It is mention that it happen is because the molecules with functional groups such as alcohol, ester, ketone and phenol are known as weaker adsorptive groups at the metal–oil and oil–water interfaces than the polar amine groups that are capable of ionizing at the interfaces. It is believed that in the present case, the investigated amine based inhibitors are absorbed on metal surface and protect corrosion attack by forming a barrier. Thus the inhibitors reduce corrosion rate.

4.5 Visual Inspection on the solutions

Figure 4.5 shows the color of as-received pure diesel and biodiesel, and biodiesels presence of different corrosion inhibitors (physical change in color of B20 test solution with and without corrosion inhibitors). Based on the observation, it is seen that there is a variation in the color of appearance for different biodiesel blends where higher blends of biodiesel contents appears to be lighter in colors. Biodiesel blends with the presence of corrosion inhibitors BTA shows the least difference in appearance when compared to TBA. This variation is mainly due to the rate of metallic ion dissolution within the test solution.

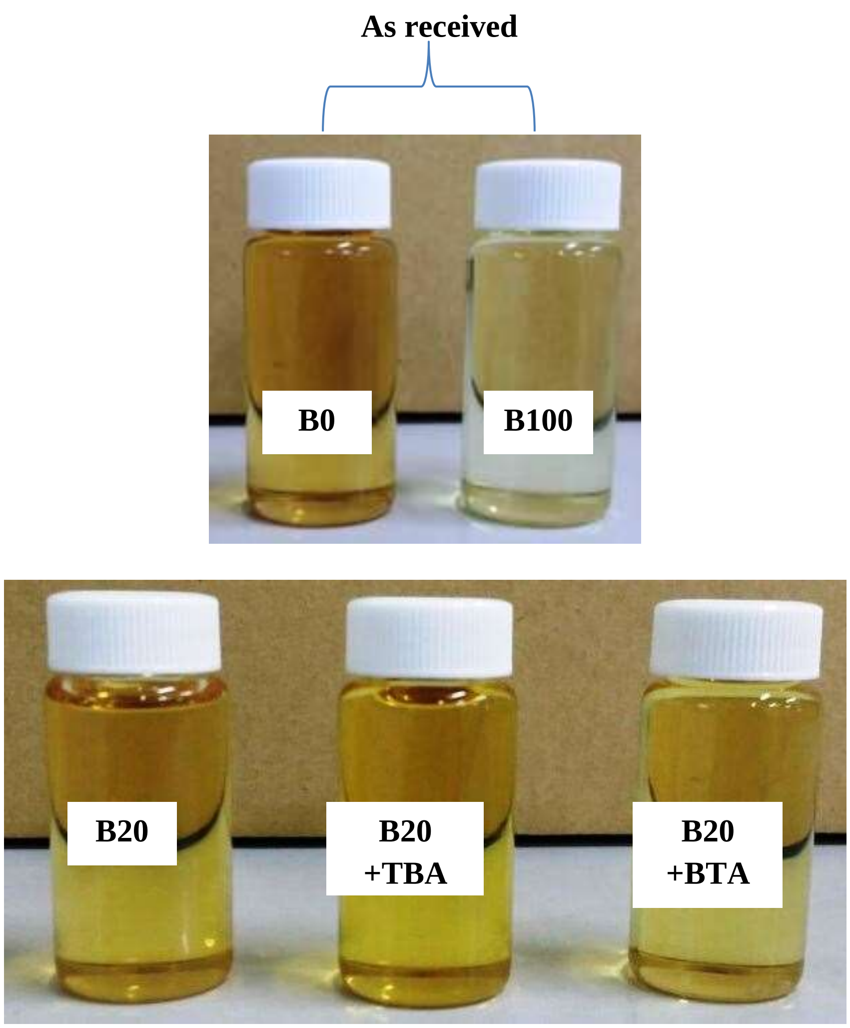
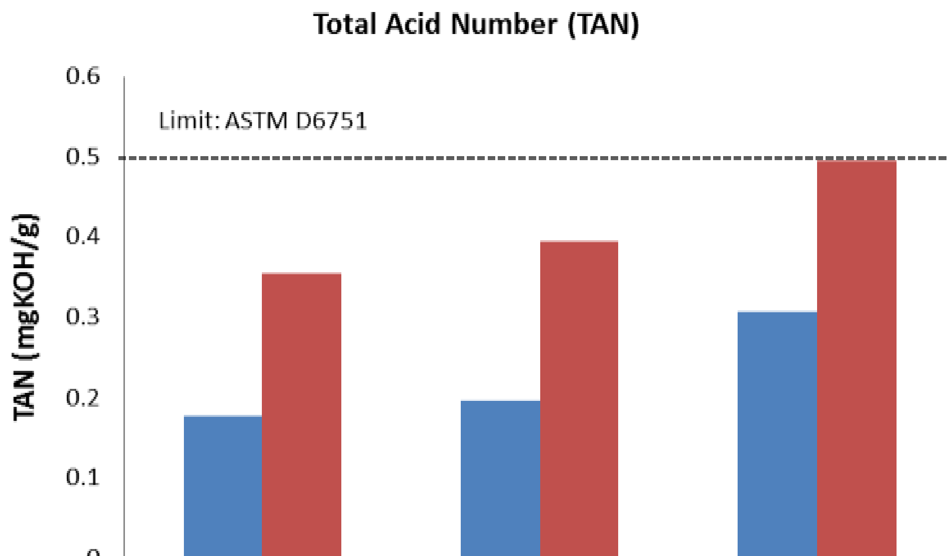


Figure 4.5: Color of as-received pure diesel and biodiesel, and biodiesels presence of different corrosion inhibitors.

4.6 Total Acid Number (TAN)

The standard limit of TAN value in biodiesel blend stocks is 0.5mg KOH/g, as per ASTM D6751. This represents the content of fatty acid within the solution. Figure 4.6.1 shows the TAN value recorded before and after immersion for B0, B20 and B100 biodiesel blends. The TAN analysis shows that the blends of B0, B20 and B100 are well and below the standard limit of 0.5mg KOH/g. Though, there is an increase in the overall TAN value after immersion testing. The trend also shows that TAN value increases with increasing biodiesel content in the immersion solution.



	B0	B20	B100
Before	0.178	0.196	0.306
After	0.355	0.395	0.496

Figure 4.6.1: Change in TAN of different biodiesel blends, before and after immersion testing

Figure 4.13 compares the TAN value recorded for B20 and B100 solution, with and without the presence of corrosion inhibitors, TBA and BTA. Based on the results, it is seen that there is a decreasing trends in the TAN value for both B20 and B100, with the addition of corrosion inhibitor. It is also noted that the test solution with BTA addition shows the least decrement in TAN value when compared to the fuel without corrosion inhibitors.

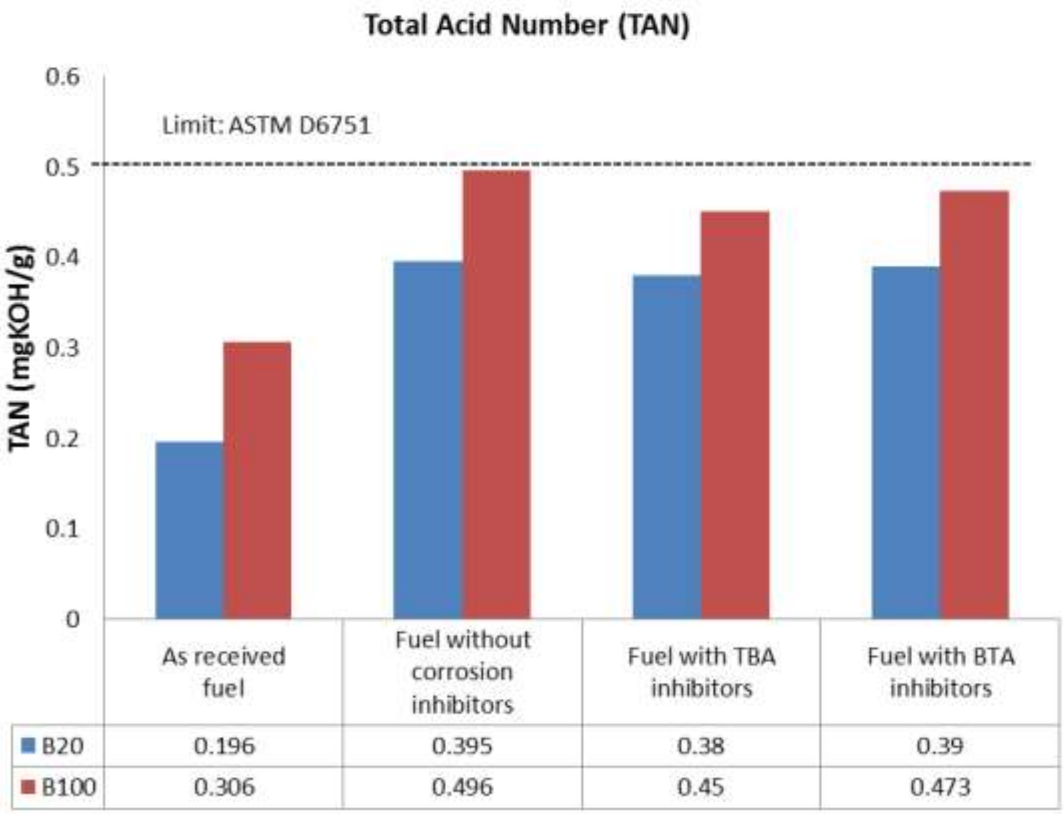


Figure 4.6.2: Comparison of change in TAN of B20 and B100 solution, with and without the presence of corrosion inhibitors, TBA and BTA

The generation of acid number upon exposure to low carbon steel S45C in biodiesel can increase the TAN value and accelerate the corrosion attack on the metal surfaces. Corrosion inhibitors are mainly amine based (base) and so they react with acid components in biodiesel. Thus they are comparatively more effective in reducing acidity of biodiesel. Yet, the results might differ from one material to another.

4.7 Density Measurement

The standard density of as-received diesel is 0.842 g/cm3, while the standard density of as-received biodiesel is 0.875 g/cm3. Figure 4.7.1 shows the density measurement of different biodiesel blends, B0, B20, B50 and B100 before and upon complete immersion testing. The results indicate that the increasing biodiesel content from B0 to B100 increases the density of the test solution. B0 that is pure diesel solution shows the least increase in the density of the test solution. It also shows that as-received diesel have lower density value compared with the density value upon immersion test.

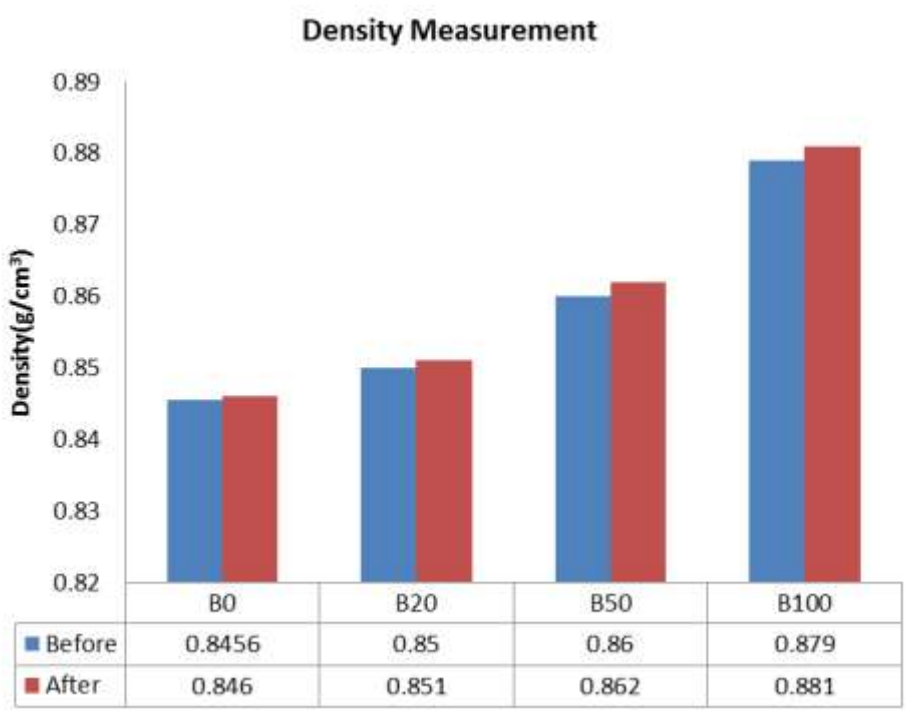


Figure 4.7.1: Change in density of different biodiesel blends upon complete immersion testing

Figure 4.7.2 shows the density measurement of B20 and B100 biodiesel blends with and without TBA and BTA corrosion inhibitors. Based on the results, it is seen that there is a decreasing trend in the density of the test solution with the addition of corrosion inhibitors. The addition of TBA inhibitors tends to be more effective in reducing the density of the biodiesel blends when compared to the addition of BTA inhibitors.

This finding is supported by the similar decreasing trend seen through TAN analysis, thus proving that the addition of corrosion inhibitors, particularly TBA is a practical solution for corrosion prevention of low carbon steel S45C in the biodiesel environment.

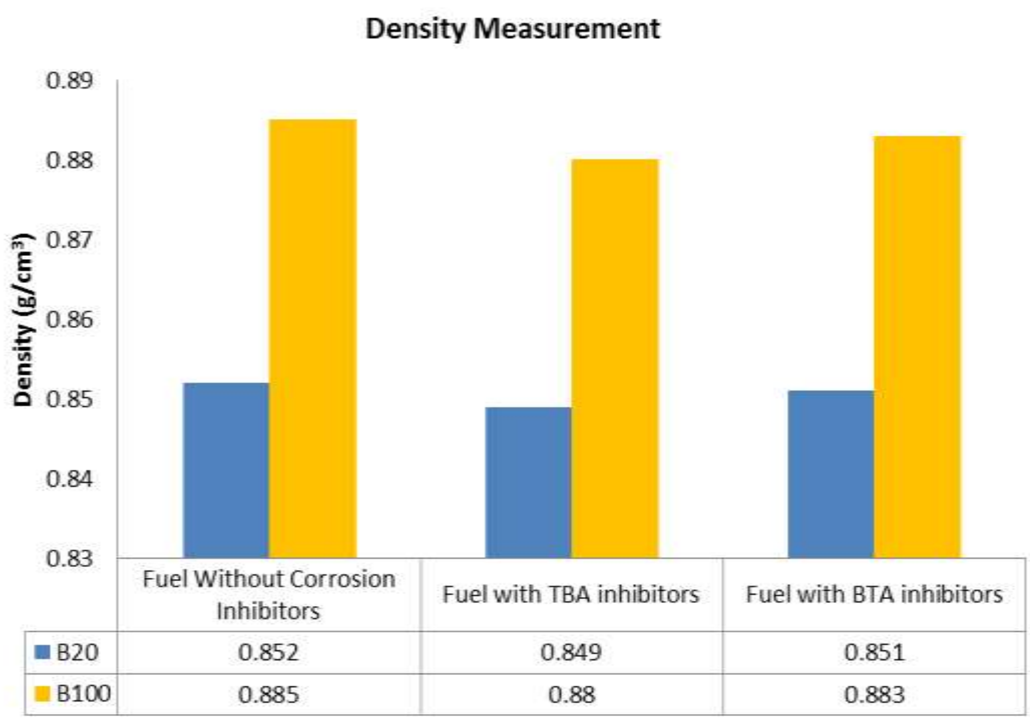


Figure 4.7.2: Comparison of density of B20 and B100 biodiesel blends with and without TBA and BTA corrosion inhibitors

CHAPTER 5

CONCLUSIONS & RECOMMENDATIONS

5.0 Conclusions

The results of the present investigation have led to the following conclusions:

i. Increasing blends of biodiesel increases the corrosion rate of low carbon steel S45C.

ii. The investigated corrosion inhibitors showed different levels of corrosion inhibition for low carbon steel S45C. TBA was found as the most effective corrosion inhibitor compared to BTA.

iii. Inhibition of corrosion by inhibitors is more likely attributed to the adsorption of inhibitor molecules onto reactive sites on the metal surface preventing contact of oxygen or water through formation of adherent oxide layers. It is believed that formation of iron nitrate hydrate due to chemisorption of TBA reduces corrosion rate by preventing further metal oxide formation and dissolution.

5.1 Recommendations

Throughout this research, it is recommended to add some steps as below in order to get more accurate results.

1. To use thicker test samples to improve timing on sample preparation and prevent researcher from injury problems.
2. To tightly closed the beaker with shrink wrap material to prevent contamination and moisture from affecting the immersion test process.
3. Increase number of test sample, thus statistical tools analysis can be implemented in the research.
4. Increasing immersion time to achieve better observation and reaction between the test samples and solutions.
5. To perform more data analysis such as X-Ray Diffraction (XRD) study on the test sample.
6. To use various type of corrosion inhibitors in order for better evaluation of the results.

REFERENCES

Agarwal, D. A. K. Performance evaluation and tribological studies on a biodiesel fuelled compression ignition engine.pdf.

Allam, N. K., Nazeer, A. A., & Ashour, E. A. (2009). A review of the effects of benzotriazole on the corrosion of copper and copper alloys in clean and polluted environments. *Journal of Applied Electrochemistry, 39*(7), 961-969. doi: 10.1007/s10800-009-9779-4

Almeida, E. S., Portela, F. M., Sousa, R. M. F., Daniel, D., Terrones, M. G. H., Richter, E. M., & Muñoz, R. A. A. (2011). Behaviour of the antioxidant tert-butylhydroquinone on the storage stability and corrosive character of biodiesel. *Fuel, 90*(11), 3480-3484. doi: 10.1016/j.fuel.2011.06.056

Annamalai, S. J. a. K. (2011). The Status of Biodiesel as an Alternative Fuel for Diesel Engine- An Overview. *Journal of Sustainable Energy & Environment, 2*, 71-75.

Aquino, I. P., Hernandez, R. P. B., Chicoma, D. L., Pinto, H. P. F., & Aoki, I. V. (2012). Influence of light, temperature and metallic ions on biodiesel degradation and corrosiveness to copper and brass. *Fuel, 102*, 795-807. doi: 10.1016/j.fuel.2012.06.011

Atabani, A. E., Silitonga, A. S., Badruddin, I. A., Mahlia, T. M. I., Masjuki, H. H., & Mekhilef, S. (2012). A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renewable and Sustainable Energy Reviews, 16*(4), 2070-2093. doi: 10.1016/j.rser.2012.01.003

Balat, M., & Balat, H. (2008). A critical review of bio-diesel as a vehicular fuel. *Energy Conversion and Management, 49*(10), 2727-2741. doi: 10.1016/j.enconman.2008.03.016

Bhale, K. A. S. a. P. V. (January 2013). Impact of biodiesel on fuel system materials durability. *Journal of Scientific & Industrial Research, 72*, 48-57.

Bouaid, A., Martinez, M., & Aracil, J. (2007). Long storage stability of biodiesel from vegetable and used frying oils. *Fuel, 86*(16), 2596-2602. doi: 10.1016/j.fuel.2007.02.014

Cursaru, D.-L., Brănoiu, G., Ramadan, I., & Miculescu, F. (2014). Degradation of automotive materials upon exposure to sunflower biodiesel. *Industrial Crops and Products, 54*, 149-158. doi: 10.1016/j.indcrop.2014.01.032

Dwivedi, G., & Sharma, M. P. (2014). Impact of cold flow properties of biodiesel on engine performance. *Renewable and Sustainable Energy Reviews, 31*, 650-656. doi: 10.1016/j.rser.2013.12.035

E. Guilminot, J. J. R., F. Dalard, C. Degrigny, X. Hiron. (2000). Benzotriazole as inhibitor for copper with and without corrosion products in aques polyethylene glycol. *Journal of Applied Electrochemistry*(30), 21-28.

Fazal, M. A., Haseeb, A. S. M. A., & Masjuki, H. H. (2010). Comparative corrosive characteristics of petroleum diesel and palm biodiesel for automotive materials. *Fuel Processing Technology, 91*(10), 1308-1315. doi: 10.1016/j.fuproc.2010.04.016

Fazal, M. A., Haseeb, A. S. M. A., & Masjuki, H. H. (2011a). Biodiesel feasibility study: An evaluation of material compatibility; performance; emission and engine durability. *Renewable and Sustainable Energy Reviews, 15*(2), 1314-1324. doi: 10.1016/j.rser.2010.10.004

Fazal, M. A., Haseeb, A. S. M. A., & Masjuki, H. H. (2011b). Effect of different corrosion inhibitors on the corrosion of cast iron in palm biodiesel. *Fuel Processing Technology, 92*(11), 2154-2159. doi: 10.1016/j.fuproc.2011.06.012

Fazal, M. A., Haseeb, A. S. M. A., & Masjuki, H. H. (2011c). Effect of temperature on the corrosion behavior of mild steel upon exposure to palm biodiesel. *Energy, 36*(5), 3328-3334. doi: 10.1016/j.energy.2011.03.028

Fazal, M. A., Haseeb, A. S. M. A., & Masjuki, H. H. (2013). Corrosion mechanism of copper in palm biodiesel. *Corrosion Science, 67*, 50-59. doi: 10.1016/j.corsci.2012.10.006

Fazal, M. A., Haseeb, A. S. M. A., & Masjuki, H. H. (2014). A critical review on the tribological compatibility of automotive materials in palm biodiesel. *Energy Conversion and Management, 79*, 180-186. doi: 10.1016/j.enconman.2013.12.002

Fazal, M. A., Jakeria, M. R., & Haseeb, A. S. M. A. (2014). Effect of copper and mild steel on the stability of palm biodiesel properties: A comparative study. *Industrial Crops and Products, 58*, 8-14. doi: 10.1016/j.indcrop.2014.03.019

Fernandes, D. M., Montes, R. H. O., Almeida, E. S., Nascimento, A. N., Oliveira, P. V., Richter, E. M., & Muñoz, R. A. A. (2013). Storage stability and corrosive character of stabilised biodiesel exposed to carbon and galvanised steels. *Fuel, 107*, 609-614. doi: 10.1016/j.fuel.2012.11.010

Finšgar, M., & Milošev, I. (2010). Inhibition of copper corrosion by 1,2,3-benzotriazole: A review. *Corrosion Science, 52*(9), 2737-2749. doi: 10.1016/j.corsci.2010.05.002

Geller, D. P., Adams, T. T., Goodrum, J. W., & Pendergrass, J. (2008). Storage stability of poultry fat and diesel fuel mixtures: Specific gravity and viscosity. *Fuel, 87*(1), 92-102. doi: 10.1016/j.fuel.2007.03.043

H.N.Meenakshi, A. A., R.Shyamala, R.Saratha. (2010). Corrosion of Metals in Biodiesel from Pongamia Pinnata.

Haseeb, A. S. M. A., Fazal, M. A., Jahirul, M. I., & Masjuki, H. H. (2011). Compatibility of automotive materials in biodiesel: A review. *Fuel, 90*(3), 922-931. doi: 10.1016/j.fuel.2010.10.042

Haseeb, A. S. M. A., Masjuki, H. H., Ann, L. J., & Fazal, M. A. (2010). Corrosion characteristics of copper and leaded bronze in palm biodiesel. *Fuel Processing Technology, 91*(3), 329-334. doi: 10.1016/j.fuproc.2009.11.004

Hoekman, S. K., Broch, A., Robbins, C., Ceniceros, E., & Natarajan, M. (2012). Review of biodiesel composition, properties, and specifications. *Renewable and Sustainable Energy Reviews, 16*(1), 143-169. doi: 10.1016/j.rser.2011.07.143

Hu, E., Xu, Y., Hu, X., Pan, L., & Jiang, S. (2012). Corrosion behaviors of metals in biodiesel from rapeseed oil and methanol. *Renewable Energy, 37*(1), 371-378. doi: 10.1016/j.renene.2011.07.010

J.Kaminski, K. J. K. (2008). USE OF IMPEDANCE SPECTROSCOPY TO TESTING CORROSION RESISTANCE OF CARBON STEEL AND STAINLESS STEEL IN

WATER-BIODIESEL CONFIGURATION. *Journal of Corrosion Measurements (JCM), 6*.

J.M. Nzikou, L. M., J.E. Moussounga, etc. (2009). Study of oxidative and thermal stability of vegetable oils during frying.pdf. *Research Journal of Applied Science*.

Jain, S., & Sharma, M. P. (2011). Thermal stability of biodiesel and its blends: A review. *Renewable and Sustainable Energy Reviews, 15*(1), 438-448. doi: 10.1016/j.rser.2010.08.022

Jakeria, M. R., Fazal, M. A., & Haseeb, A. S. M. A. (2014). Influence of different factors on the stability of biodiesel: A review. *Renewable and Sustainable Energy Reviews, 30*, 154-163. doi: 10.1016/j.rser.2013.09.024

Karmakar, A., Karmakar, S., & Mukherjee, S. (2010). Properties of various plants and animals feedstocks for biodiesel production. *Bioresour Technol, 101*(19), 7201-7210. doi: 10.1016/j.biortech.2010.04.079

Khan, P. F., Shanthi, V., Babu, R. K., Muralidharan, S., & Barik, R. C. (2015). Effect of benzotriazole on corrosion inhibition of copper under flow conditions. *Journal of Environmental Chemical Engineering, 3*(1), 10-19. doi: 10.1016/j.jece.2014.11.005

Kosec, T., Milošev, I., & Pihlar, B. (2007). Benzotriazole as an inhibitor of brass corrosion in chloride solution. *Applied Surface Science, 253*(22), 8863-8873. doi: 10.1016/j.apsusc.2007.04.083

Lei, Y. H., Sheng, N., Hyono, A., Ueda, M., & Ohtsuka, T. (2014). Effect of benzotriazole (BTA) addition on Polypyrrole film formation on copper and its corrosion protection. *Progress in Organic Coatings, 77*(2), 339-346. doi: 10.1016/j.porgcoat.2013.10.009

Marcos Alberto Coronado Ortega, G. M. A., Amir Eliezer, Conrado Garcia Gonzalez, Jesus Cerezo Roman, Laura Janet Perez Pelayo, Jose Ramon Ayala Bautista (2013). Materials technological challenges for the biodiesel industry development in Mexico *Energy materials book* (pp. 279-288). Mexico: Formatex.

Marta A. Jakab, S. R. W., Scott A. Hutzler. (2008). TESTING FOR COMPATIBILITY OF STEEL WITH BIODIESEL: SOUTHWEST RESEARCH INSTITUTE.

Maru, M. M., Lucchese, M. M., Legnani, C., Quirino, W. G., Balbo, A., Aranha, I. B., . . . Achete, C. A. (2009). Biodiesel compatibility with carbon steel and HDPE parts. *Fuel Processing Technology, 90*(9), 1175-1182. doi: 10.1016/j.fuproc.2009.05.014

Ong, H. C., Mahlia, T. M. I., Masjuki, H. H., & Norhasyima, R. S. (2011). Comparison of palm oil, Jatropha curcas and Calophyllum inophyllum for biodiesel: A review. *Renewable and Sustainable Energy Reviews*, *15*(8), 3501-3515. doi: 10.1016/j.rser.2011.05.005

P. Li, J. Y. L., K. L. Tan and J. Y. Lee. (1997). Electrochemical impedance and X-ray photoelectron spectroscopic studies of the inhibition of mild steel corrosion in acids by cyclohexylamine. *42*, 605-615.

Parameswaran, M. H. N., Anand, A., & Krishnamurthy, S. R. (2013). A Comparison of Corrosion Behavior of Copper and Its Alloy in Pongamia pinnata Oil at Different Conditions. *Journal of Energy, 2013*, 1-4. doi: 10.1155/2013/932976

Rashedul, H. K., Masjuki, H. H., Kalam, M. A., Ashraful, A. M., Ashrafur Rahman, S. M., & Shahir, S. A. (2014). The effect of additives on properties, performance and emission of biodiesel fuelled compression ignition engine. *Energy Conversion and Management, 88*, 348-364. doi: 10.1016/j.enconman.2014.08.034

Ravichandran, R., Nanjundan, S., & Rajendran, N. (2004). Effect of benzotriazole derivatives on the corrosion of brass in NaCl solutions. *Applied Surface Science, 236*(1-4), 241-250. doi: 10.1016/j.apsusc.2004.04.025

Sgroi, M., Bollito, G., Saracco, G., & Specchia, S. (2005). BIOFEAT: Biodiesel fuel processor for a vehicle fuel cell auxiliary power unit. *Journal of Power Sources, 149*, 8-14. doi: 10.1016/j.jpowsour.2004.12.059

Singh, B., Korstad, J., & Sharma, Y. C. (2012). A critical review on corrosion of compression ignition (CI) engine parts by biodiesel and biodiesel blends and its inhibition. *Renewable and Sustainable Energy Reviews*, *16*(5), 3401-3408. doi: 10.1016/j.rser.2012.02.042

Torsner, E. (2010). Solving corrosion problems in biofuels industry. *Corrosion Engineering, Science and Technology, 45*(1), 42-48. doi: 10.1179/147842209x12579401586726

Tyson. (September 2001). BIODIESEL Handling & Use Guidlines.

Yaakob, Z., Narayanan, B. N., Padikkaparambil, S., Unni K, S., & Akbar P, M. (2014). A review on the oxidation stability of biodiesel. *Renewable and Sustainable Energy Reviews, 35*, 136-153. doi: 10.1016/j.rser.2014.03.055

Yıldırım, A., & Çetin, M. (2008). Synthesis and evaluation of new long alkyl side chain acetamide, isoxazolidine and isoxazoline derivatives as corrosion inhibitors. *Corrosion Science, 50*(1), 155-165. doi: 10.1016/j.corsci.2007.06.015